VOL. LV, NO. 10, OCTOBER, 1960

THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS ASSOCIATION
PUBLICATION OFFICE, EASTON, PA.

"LUNA"
BRAND

cold water soluble in solid or seco crushed

"SUPREMO"
BRAND

ordinary in solid or seco crushed

The oldest American manufacturer of extracts in South America. Factories at Puerto Pinasco, Paraguay, and Staten Island, N. Y.

Liquid and powdered extract and blends to specifications in bags, barrels, tank cars or tank trucks from warehouse stocks at Arlington, Staten Island, N. Y.

International Products Corporation
Executive Office
625 Madison Avenue, New York 22, N. Y.
Telephone: Plaza 1-4770

The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV OCTOBER 1960 No. 10

CONTENTS

The Depolymerization of Collagen Fibers - - - - - - - - *By* A. Veis, J. Anesey, and J. Cohen **548**

The Temperature Dependence of the Breaking of Hydrogen Bonds of Collagen by Urea and Some of Its Implications - - - - - - - - *By* K. H. Gustavson **564**

Life Lines - - - - - - - - - - - - **585**

ALCA News - - - - - - - - - - - - **586**

Abstracts - - - - - - - - - - - - **588**

Patents - - - - - - - - - - - - **593**

Book Review - - - - - - - - - - - - **598**

SUBSCRIPTION - - MEMBERS $12.00 A YEAR - - NONMEMBERS $15.00

Published Monthly by

The American Leather Chemists Association

Entered as Second-Class Matter at the Post Office, Easton, Pa.
Acceptance for mailing at special rate of postage as provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918

COPYRIGHT, 1960, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices and Plant
ERIE, PA.

When leather looks like this sodium sulfhydrate helped

Unhair with a low-alkalinity bath and you get a tighter leather—soft, smooth, beautiful as only the choicest leather can be.

Hooker sodium sulfhydrate gives you this tight control better than any other sharpening agent you can buy.

Write for your copy of our Bulletin 510, a new 16-page illustrated guide to selecting and using Hooker chemicals in your work.

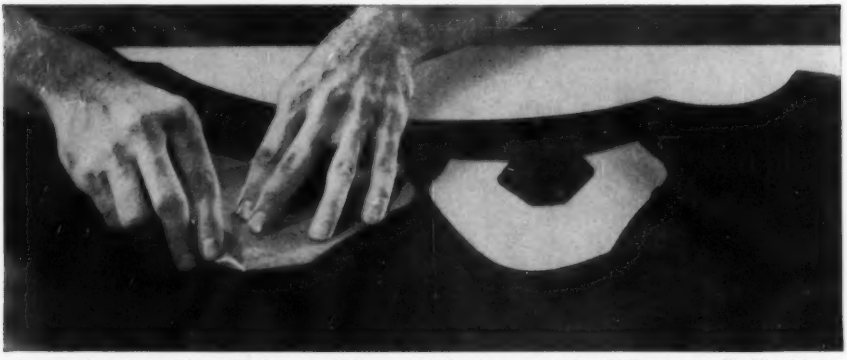
HOOKER CHEMICAL CORPORATION
910 UNION STREET, NIAGARA FALLS, N. Y.

Sales Offices: Buffalo Chicago Detroit Los Angeles New York Niagara Falls Philadelphia Tacoma Worcester, Mass.
In Canada: Hooker Chemicals Limited, North Vancouver, B. C.

HOOKER CHEMICALS PLASTICS

Upgrades leather quality

ZIRCOTAN T



Cutting shoe uppers from flank area of chrome side leather retanned with ZIRCOTAN T. *No, it's no mistake. Solidity of flank section closely approaches the quality of leather nearer back bone edge.*

ZIRCOTAN T offers you the double advantages of improved results and greater uniformity of quality in the tanning of fine leathers.

Chrome-tanned leather, retanned with ZIRCOTAN T, is tighter, fuller, more solid and has better flanks. ZIRCOTAN T helps produce a finer break and gives the leather a particularly fine nap when buffed.

Used alone, ZIRCOTAN T is unsurpassed in the preparation of premium quality white leather which is uniformly white through its entire thickness. The finished leather is stable to prolonged washing with water, maintains its strength and leather character on aging, and does not lose its white color on exposure to sunlight.

Request complete information on ZIRCOTAN T from the Leather Chemicals Department of Rohm & Haas, or call your local representative.

ZIRCOTAN *is a trademark, Reg. U.S. Pat. Off. and in principal foreign countries.*

Facts about versatile, low-cost ZIRCOTAN T... to help you bring out and protect all the quality your leather can deliver.

Chemicals for Industry

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

from Tannery Wheels to Finished Leathers

THE RESULTS OF

Mardol

. . . The results of Mardol tannery oils and fat liquors in modern leather making, are seen in the finished product. Oil blending by specialists, laboratory and quality control, backed up by chemistry "know-how," and services of our own technical tanning staff, all contribute to the making of better leather.

MARDEN-WILD CORPORATION

500 COLUMBIA ST., SOMERVILLE, MASS.

MILWAUKEE, WISCONSIN, 8934 NO. NAVAJO AVE.
MARDEN-WILD OF CANADA LTD., HALIFAX, N. S.

FRENCH

CHESTNUT EXTRACT

SOLID: 62%—GROUND POWDER: 64, 68%—SPRAY-DRIED POWDER: 67, 70, 72%

★ **PROGIL S.A. and TANNINS REY S.A.,** world-known producers, concentrate production of copper-free extract in up-to-date, specially equipped factories to assure you *continuous uniformity in quality* in every shipment you get—month after month, year after year. Expert technical aid available from both sides of the Atlantic.

order from TAC

TAC

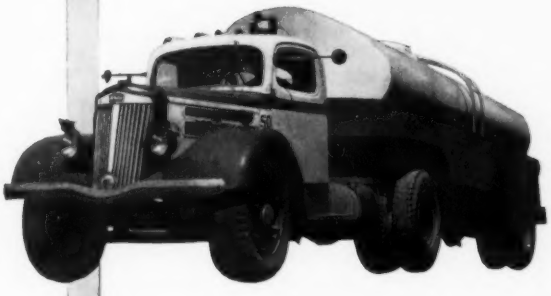
TANNINS & CHEMICALS, INC.

509 MADISON AVE., NEW YORK 22 ★ MU 8-9240

Midwest Branch: 327 So. LaSalle St., Chicago 4, Ill. ★ WA 2-8900

TRASK
EST. 1924

Caught Short?
Call TRASK!



Our stainless steel tank truck or tank car will be, most times, at your plant the morning after your call for:

CHESTNUT EXTRACT
QUEBRACHO EXTRACT • WAXES
SULFONATED OILS • STUFFING
GREASES • LIGNOSULFONATES
CHEMICAL SPECIALTIES

ARTHUR C. TRASK CO.

327 S. LaSalle St., Chicago 4, Ill.
WAbash 2-8900
509 Madison Ave., New York 22, MU 8-9240
67 Farningham, Islington, Ont., Canada, BE 3-6582

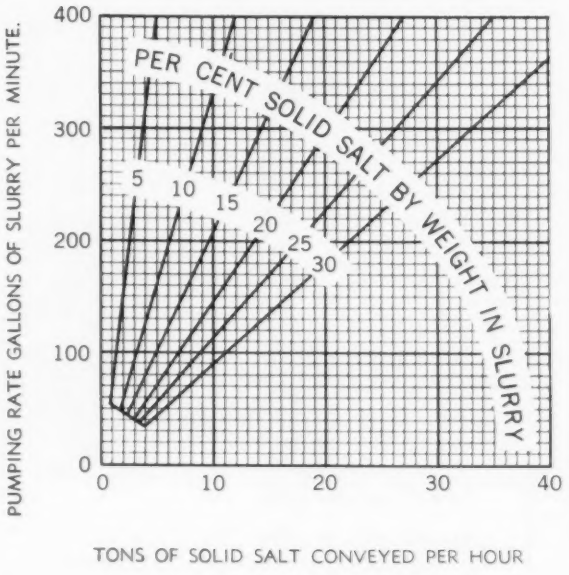
CABLE: *Actrask* TELETYPE: CG 1478

Using Salt Efficiently

by **INTERNATIONAL SALT COMPANY**

Unloading and Storing Bulk Salt in One Operation . . . by Hydraulic Handling

Many companies faced with the need to unload and store large shipments of bulk salt have installed Hydraulic Handling systems. In these systems, salt delivered by car, truck or barge is dumped into a pit and mixed with saturated brine. The slurry is then pumped into a wet salt-storage tank. Overflow carrier brine returns to the pit to carry more salt into storage. The operation, besides being continuous, also offers these important benefits:



Hydraulic Handling can move salt any distance. Because the necessary piping is flexible and can be installed anywhere, there's no need to move existing equipment or disrupt important operations. Hydraulic Handling is dustless, safe, and more economical than many mechanical handling systems. One man can operate it. Maintenance is negligible. And, to handle larger salt shipments as production increases, the system can be expanded at nominal expense.

While any Hydraulic Handling installation provides these benefits in some degree, only sound engineering can assure 100% efficiency and economy. That's where International Salt Company can help. One of our experienced sales engineers can supply detailed data on functional pit designs, correct pump types and capacities, and durable pipelines and valves.

He can also furnish information on minimum clogging and settling velocities . . . liquid-level controls for slurrying pits . . . dilution valves for proper slurry make-up . . . and many other factors that go to make an efficient, trouble-free Hydraulic Handling system.

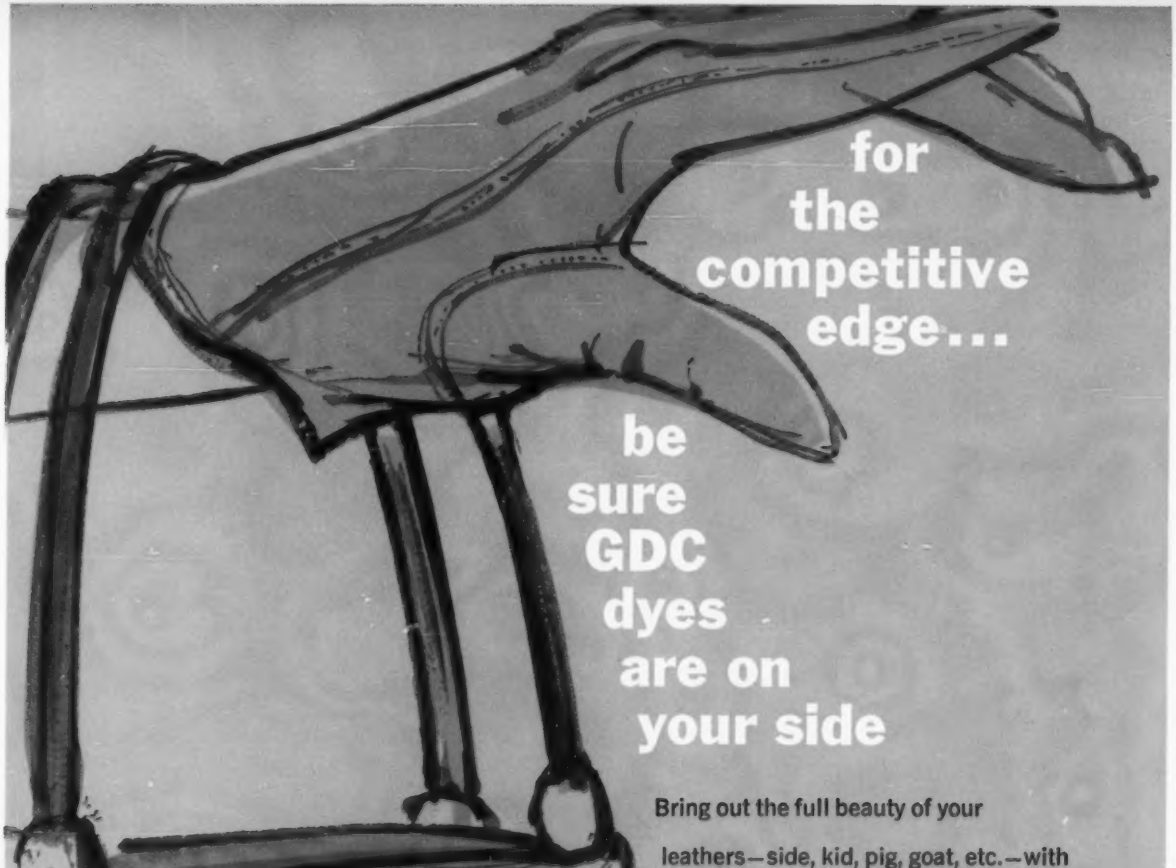
To get this expert professional help — as well as information on any problem concerning salt or brine — contact your nearest International Salt Company sales office.

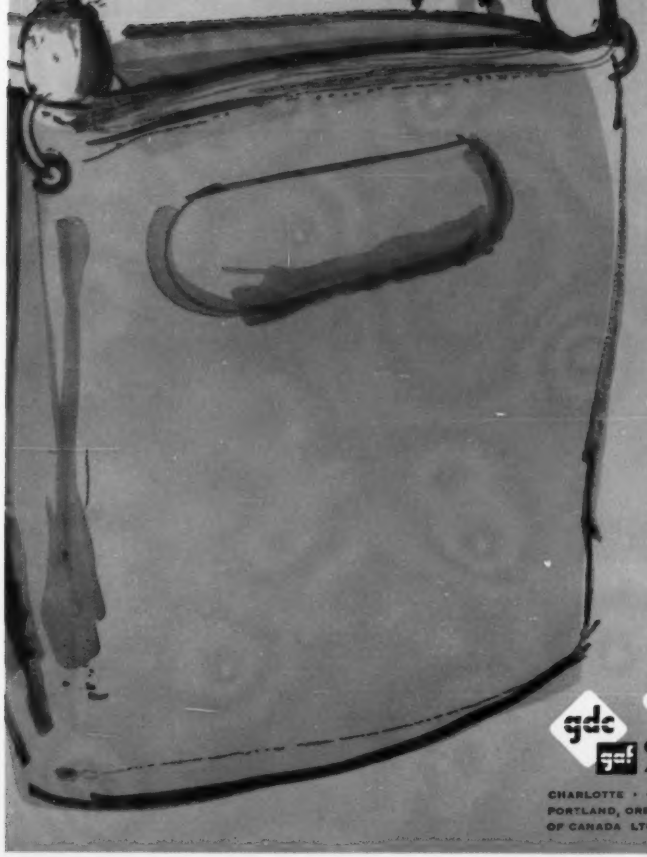
INTERNATIONAL SALT COMPANY
CLARKS SUMMIT, PA.

SALES OFFICES

Boston	Cincinnati	New York
Buffalo	Detroit	Philadelphia
Charlotte	Newark	Pittsburgh
Chicago	New Orleans	St. Louis

Service and research are the extras in STERLING SALT
PRODUCT OF INTERNATIONAL SALT COMPANY


for
the
competitive
edge...
be
sure
GDC
dyes
are on
your side
Bring out the full beauty of your
leathers—side, kid, pig, goat, etc.—with



leathers—side, kid, pig, goat, etc.—with GDC DYES. You can select dyes that will produce the extra attention-getting, sales-stimulating, in-fashion shades so essential in today's competitive market.

Contact the GDC Technical Service Representative nearest you and discover how GDC DYES for leather can do a better job for you and help keep you ahead of competition.

gdc gaf

GENERAL DYESTUFF COMPANY

A SALES DIVISION OF

GENERAL ANILINE & FILM CORPORATION

435 HUDSON STREET · NEW YORK 14, NEW YORK

CHARLOTTE · CHATTANOOGA · CHICAGO · LOS ANGELES · NEW YORK · PHILADELPHIA
PORTLAND, ORE. · PROVIDENCE · SAN FRANCISCO · IN CANADA: CHEMICAL DEVELOPMENTS OF CANADA LTD., MONTREAL

FOR HIGHEST LEATHER LUSTRE

Mearlmaid NATURAL PEARL ESSENCE

Mearlmaid Pearl Essence is a completely organic product—it will not discolor on exposure to sulfides during processing or use. You are assured a lustre of durable beauty, which can be guaranteed to stay that way.

Mearlmaid Pearl Essence is available in several qualities to meet your specific lustre and cost requirements. See the difference Mearlmaid Pearl Essence will make in your leathers.

WHERE COST IS THE MAJOR FACTOR, Nacromer synthetic pearl essence provides an equal lustre at a fraction of the cost.

NEW!

MURANO® COLORS

LUSTROUS SYNTHETIC PEARL IN BEAUTIFUL COLORS

Here are colors produced by optical effect...colors inherent in the crystalline structure of the pearl...colors with reflection and transmission complements. Murano Colors provide multiple color play verging on the iridescent effects impossible to achieve with conventional dyes or pigments. Try it for strikingly beautiful lustrous effects.

FREE!

8-PAGE NACREOUS PIGMENT HANDBOOK

A valuable guide to the use of natural pearl essence and synthetic pearl pigments.

4-PAGE MURANO COLORS BROCHURE

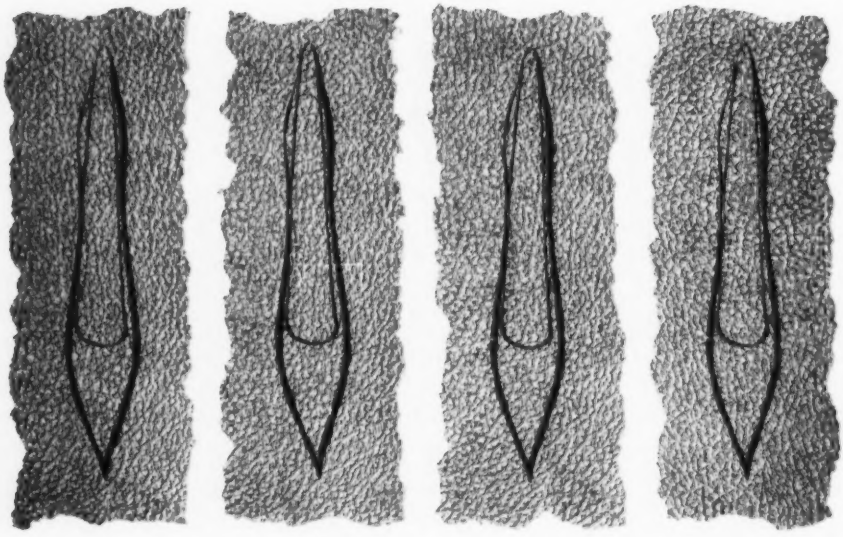
What it is... how it's used... what it does.

THE MEARL CORPORATION

world's leading producers of pearl essence

41 EAST 42nd STREET • NEW YORK 17, NEW YORK

UNIFORM RESULTS DEPEND



ON UNIFORM CHEMICALS

Top-grade tanning results every time . . . when you depend on Diamond quality chemicals: Tanolin®, fat liquors, bichromates, neutralizers.

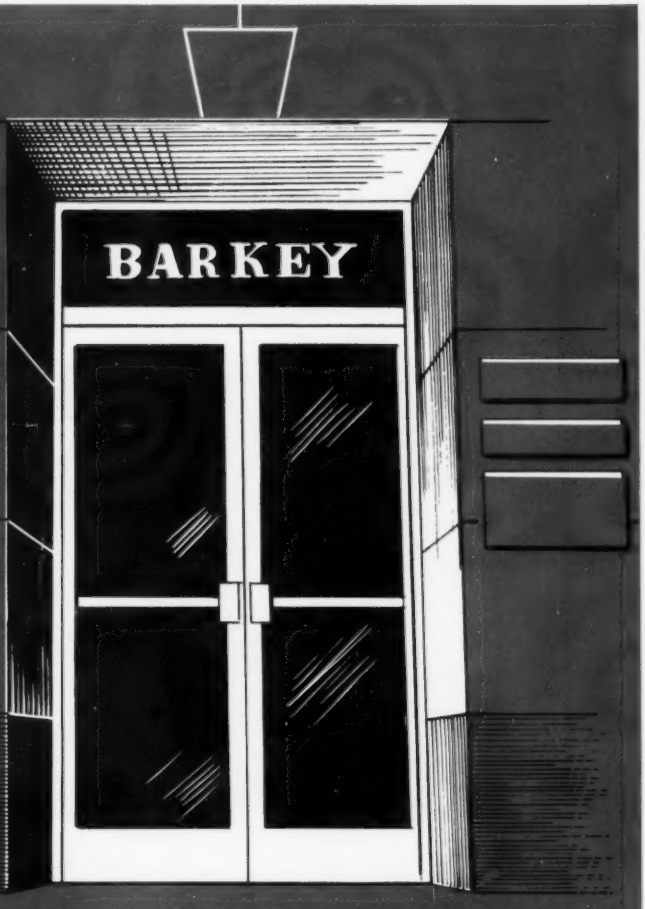
Top-notch leathermakers all over the world rely on Diamond uniform chemicals, made from the finest raw materials, quality controlled every step of the way.

So why not you? You'll get fast, dependable delivery on every order you place from our two plants, or from eight strategically located warehouses. And Diamond's long experience in working with quality tanners to achieve best results is yours for the asking.

Your Diamond Representative knows leather chemistry . . . and he's backed by Diamond's entire technical staff and facilities. Call him today. DIAMOND ALKALI COMPANY, 300 Union Commerce Building, Cleveland 14, Ohio.

Diamond® Chemicals

AMERICA'S
OLDEST
and
LARGEST
EXCLUSIVE
IMPORTERS



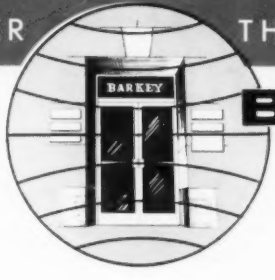
VEGETABLE
TANNING
MATERIALS

—Quebracho...Wattle...Chestnut
and all other extracts...
in solid, crushed, ground and spray-dried.
—also raw materials for leaching.

FROM ALL OVER THE WORLD

Europe...Asia...Africa...
South America...Central America.

Cable address
JABARKEY



BARKEY
Importing Company, Inc.

DIRECT IMPORTERS OF
VEGETABLE TANNING MATERIALS.

44 East 53rd Street • New York 22, New York

SANDOZ

THINKS AHEAD WITH LEATHER

– See SANDOZ

SANDOZ technicians—with laboratory and pilot-scale facilities at their finger-tips—have achieved over a long period of experimental years a proven record of "Know-How". The result: Today they can offer the most advanced knowledge in the business when it comes to "How-To" in solving leather coloring problems.

Every Sandoz leather representative is ready and able to run tannery trials with new products, and to assist with tannery questions whenever and wherever they may arise. As a matter of fact, several tanneries have sent personnel to our laboratories for training in coloring or to oversee the working out of their own problems.

So keep in mind: If you require "How-To" in addition to "Know-How"—write, wire, or phone SANDOZ, INC., 61-63 Van Dam St., New York 13, New York, ALgonquin 5-1700.

District Offices: Charlotte, Cincinnati, Fair Lawn, N. J., Hudson, Mass., Los Angeles, Philadelphia.

ARKOTAN®

PRETANS:	for smoother grain, more leather yield
BLEACHES:	chrome white leathers
STAINS:	suede crust leathers for light color, tight nap
AIDS:	bark tanning of light leathers
MORDANTS DYES:	for level coloring

ARKOTAN B

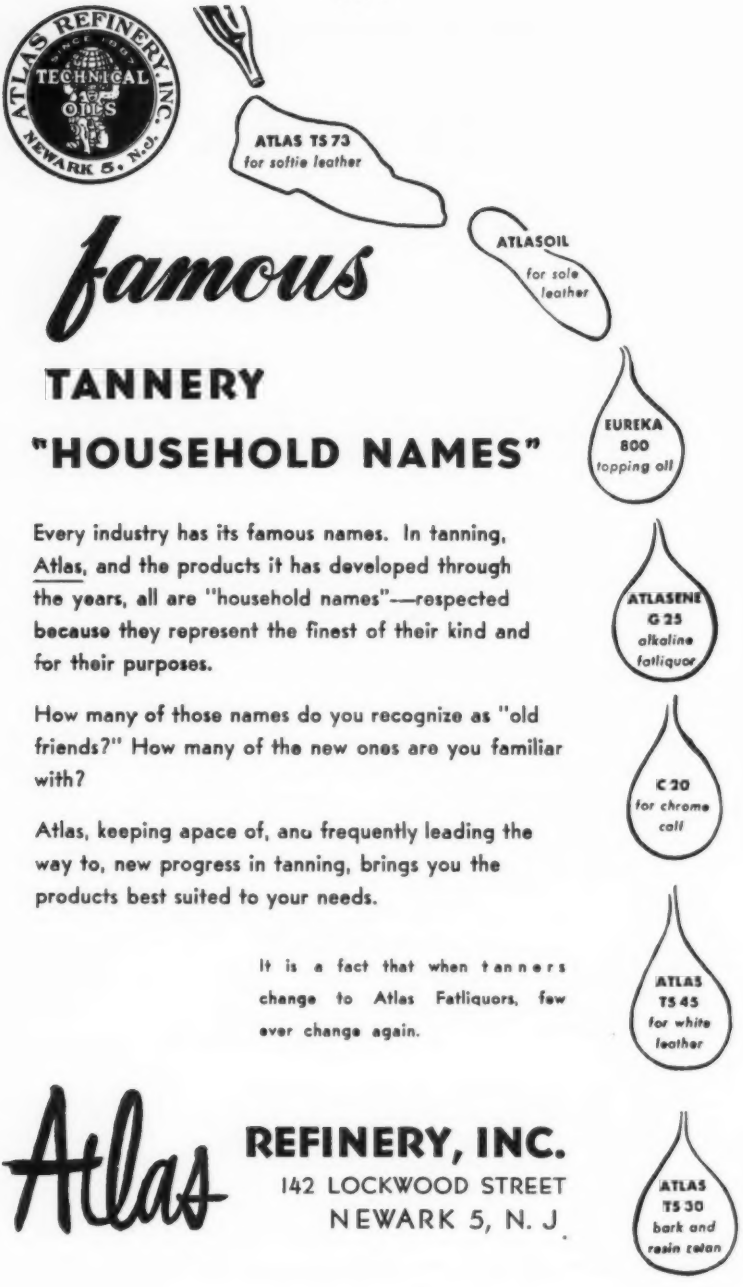
ACCELERATES:	penetration and takeup of bark tan extracts in heavy leathers
BLEACHES:	heavier chrome leathers for whites
SEQUESTERS:	mineral agents in water, for clean tanning
TIGHTENS BREAK:	gives fuller feel, smooth grain, even color in heavy bark and retan leathers

WRITE FOR TECHNICAL SERVICE BULLETIN

ARKANSAS CO., INC.

Serving the tanning industry for over 55 years

NEWARK, NEW JERSEY



Every industry has its famous names. In tanning, Atlas, and the products it has developed through the years, all are "household names"—respected because they represent the finest of their kind and for their purposes.

How many of those names do you recognize as "old friends?" How many of the new ones are you familiar with?

Atlas, keeping apace of, and frequently leading the way to, new progress in tanning, brings you the products best suited to your needs.

It is a fact that when tanners change to Atlas Fatliquors, few ever change again.

Atlas **REFINERY, INC.**
142 LOCKWOOD STREET
NEWARK 5, N. J.

Bachner *has a hand in fashion*

...with KOREON chrome-tanned leather by Leavitt-Berner

A soft, beautifully chrome-tanned deerskin by Leavitt-Berner Tanning Corp. has been fashioned by C. J. Bachner & Sons, Inc. into these attractive gloves for sport and casual wear. They're best-sellers and guaranteed hand-washable.

At Leavitt-Berner, Mutual® Koreon® one-bath chrome-tan helps make the tanning operation simple and sure. Koreon is a scientifically balanced, one-bath tanning agent of uniform purity and chromic oxide content. It's a convenient-to-use, dry product which you add to water or directly to your tanning drum where it dissolves readily. You have a choice of three basicities ... Koreon M at 33-35%, Koreon B at 41-43% and Koreon X at 50-52%.

If you prefer to make your own one-bath chrome tan, Solvay can provide the technical aid and principal raw material . . . Mutual Sodium Bichromate.

For more information about Koreon and other Solvay products, or if you would like the services of a Solvay leather specialist to answer your questions about their application, mail the coupon.

OTHER SOLVAY® PRODUCTS FOR TANNERS
Solvay Ammonium Bicarbonate • Ammonium Chloride • Snowflake® Crystals
Mutual Potassium Bichromate • Mutual Sodium Chromate

Allied Chemical

SOLVAY PROCESS DIVISION
61 Broadway, New York 6, N. Y.

MUTUAL chromium chemicals are available through distributors and SOLVAY branch offices located from coast to coast.

SOLVAY PROCESS DIVISION 38-100
Allied Chemical Corporation
61 Broadway, New York 6, N. Y.

☐ Please send booklet "KOREON One-Bath Chrome Tan for Leather."
☐ Please have your representative phone for an appointment

Name _____ Position _____
Company _____
Address _____
City _____ Zone ____ State _____

Manufacturers of

LEATHER FINISHES

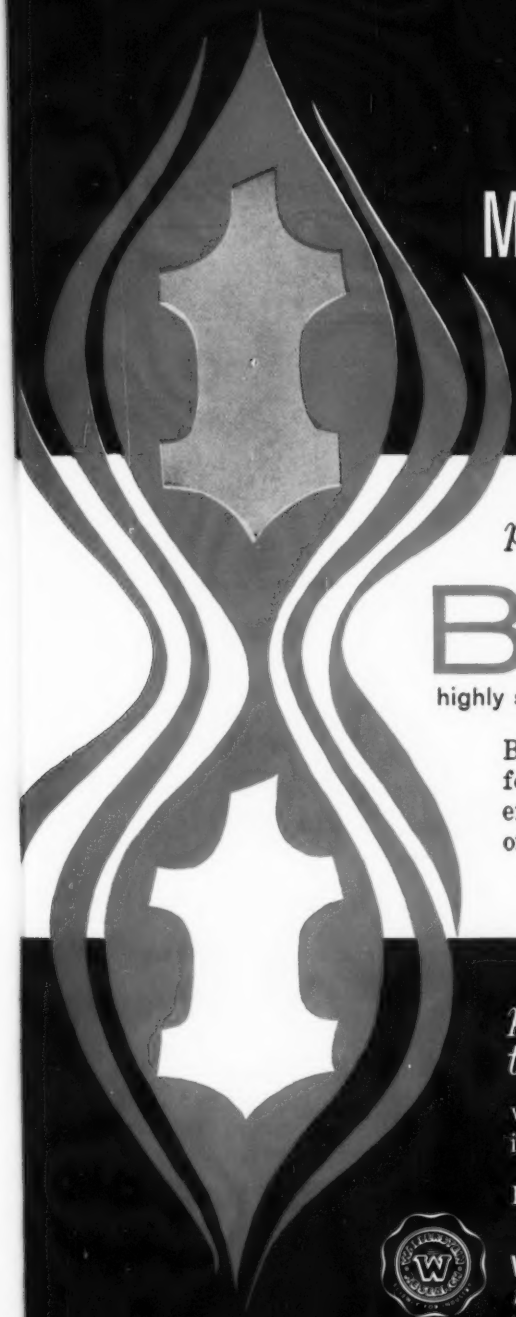
and

TANNERS' SPECIALTIES

CHEMICAL COATING MATERIALS
Company

BELLEVILLE 9 • NEW JERSEY

PLYMOUTH 9-5600



TWO STEPS THAT GIVE MAXIMUM CONTROL OF THE BATING PROCESS

processing with

BIOBATE

highly stable, standardized bating compounds

Biobates are prepared in concentrated form – provide effective, controllable enzyme action suited to all types of leather.

proper application through

WALLERSTEIN TECHNICAL SERVICE
in *your* specific tanning operations

For assurance of high grade performance.

WALLERSTEIN COMPANY
Division of Baxter Laboratories, Inc.
Wallerstein Square, Mariners Harbor
Staten Island 3, New York

also:

SEBACOL... for dependable unhairing
STEROZOL... for inhibition of bacteria and molds

TERRISS - Consolidated Industries

MANUFACTURERS SUPPLYING THE LEATHER INDUSTRY

22-24 WOOSTER STREET • NEW YORK 13, N. Y.

ALL-PURPOSE MIXERS

LABORATORY MIXER

Propeller — stainless steel, 2"
Shaft — stainless steel, ¼" diameter
RPM — variable speed, 5,000 at no load
Motor — 110V, AC, single phase, 60 cycle
Capacity — up to 5 gallons of liquid depending on viscosity
Height — 12" shaft
Weight — 15 lbs.
Delivery — immediate shipment from stock
Special Features — fully adjustable up and down and at any angle. Shipped ready to operate.

PRICE ..... $32.50 f.o.b. factory New York City

MEDIUM DUTY MIXER

Propellers — stainless steel, 4"
Shaft — stainless steel, ½" diameter
HP — 1/3
RPM — 1725
Motor — 115V, AC, single phase, 60 cycle
Capacity — up to 55 gallons of liquid depending on viscosity
Height — 36" shaft
Weight — 40 lbs.
Delivery — immediate shipment from stock
Special Features — GE Form G all-angle motor, with heavy cast iron clamp for angle adjustment. Opposite pitch propellers.

PRICE ..... $55.00 f.o.b. factory New York City

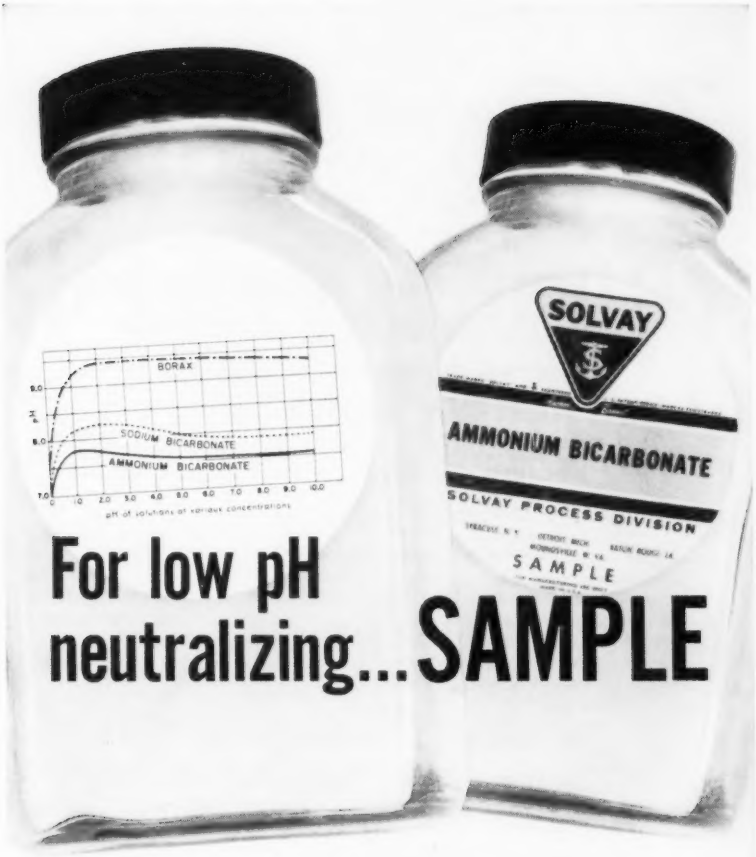
HEAVY DUTY MIXER

Propellers — stainless steel, 7"
Shaft — stainless steel, ¾" diameter
HP — 1/3
RPM — 1750 with helical gears to deliver speeds down to 430 RPM
Motor — 110V, AC, single phase, 60 cycle
Capacity — from 100 to 200 gallons of liquid depending on viscosity
Height — 48" shaft
Weight — 50 lbs.
Delivery — immediate shipment from stock
Special Features — designed for the more viscous types of liquid

PRICE ..... $99.75 f.o.b. factory New York City

A Full Range Of Agitators Are Available, Including Totally Enclosed, Explosion Proof, For Operation On Single Or Three Phase Electric Current

Agitators	Cheese Cans	Bottle Inspectors	Trucks	Measures	Pumps	Dump Buckets
Mixers	Filter Plants	Kettles	Forks	Tubing	Fittings	Pails
Surge Tanks	Milk Strainers	Shovels	Paddles	Dippers	Valves	Sinks



For low pH neutralizing...SAMPLE

Without obligation, write for a sample of Solvay® Ammonium Bicarbonate. See for yourself how *mildly* (7.8 pH) yet *thoroughly* it neutralizes your chrome-tanned leathers. Deep-penetrating—for more uniform dyeing, outstanding texture and grain.

Allied Chemical

SOLVAY PROCESS DIVISION
61 Broadway, New York 6, N. Y.

Branch Sales Offices: Boston • Charlotte • Chicago • Cincinnati • Cleveland Detroit • Houston • New Orleans • New York • Philadelphia • Pittsburgh San Francisco • St. Louis • Syracuse

The Reader Comes First

LEATHER and SHOES believes in the "Golden Rule" of journalism --serves its readers first. It has no "sacred cows" nor prejudices.

Because of this, it is first choice of the industry's key executives. L&S is the most widely read and quoted paper in its field, and leads in paid (audited) circulation, subscription and advertising receipts.

Readers and advertisers benefit most by this policy. That's why its subscription list and advertising indexes read like the Who's Who of the industry.

LEATHER and SHOES

THE MAGAZINE FOR EXECUTIVES

300 West Adams Street
CHICAGO 6, ILLINOIS

How Mobil Blends Economy into Fatliquors!

THROUGH blending petroleum chemicals with normal fatty oils and greases, Mobil has achieved fatliquors of the highest efficiency and the lowest possible cost. Here is one example.

Mobiltan O, as a result of the Mobil petroleum chemicals it contains, has these desirable characteristics: Low moisture content . . . high resistance to oxidation . . . complete freedom from spue-forming tendencies. Yet it is one of the lowest cost fatliquors offered to the tanning industry.

Mobil has a wide range of tanners products . . . each one designed to help you make better leather, *cheaper!*

There's a right Mobil product for your every tanning need

MOBILKOR—identifies a complete line of stuffing greases for use on heavy leathers, as well as work-shoe upper leathers.

MOBILFET—is the new trademark for our highly nourishing leather oils for inclusion as fatliquor additives or as finishing oils.

MOBILCROME 1—identifies a one-bath product for economical chrome tanning of all leathers.

MOBILTAN—indicates products specifically designed for application on all fatliquored leathers.

MOBILON—individually designed formulations for sole waterproofing, sponging and washing compounds.

For complete technical data on products of any of the above product groups write.
Mobil Oil Co. Inc., Tanners' Division, 150 E. 42nd St., N.Y. 17, N.Y.

Mobil

First choice of Tanners since 1866

For direct or auxiliary tanning or retanning of basic

WHITE

or chrome leather

Jacques Wolf Tanasols... Synektans... Monotans

Synthetic tannins from Jacques Wolf offer excellent light fastness, better weight, smooth grain, and full tight flanks. Write for free catalog.

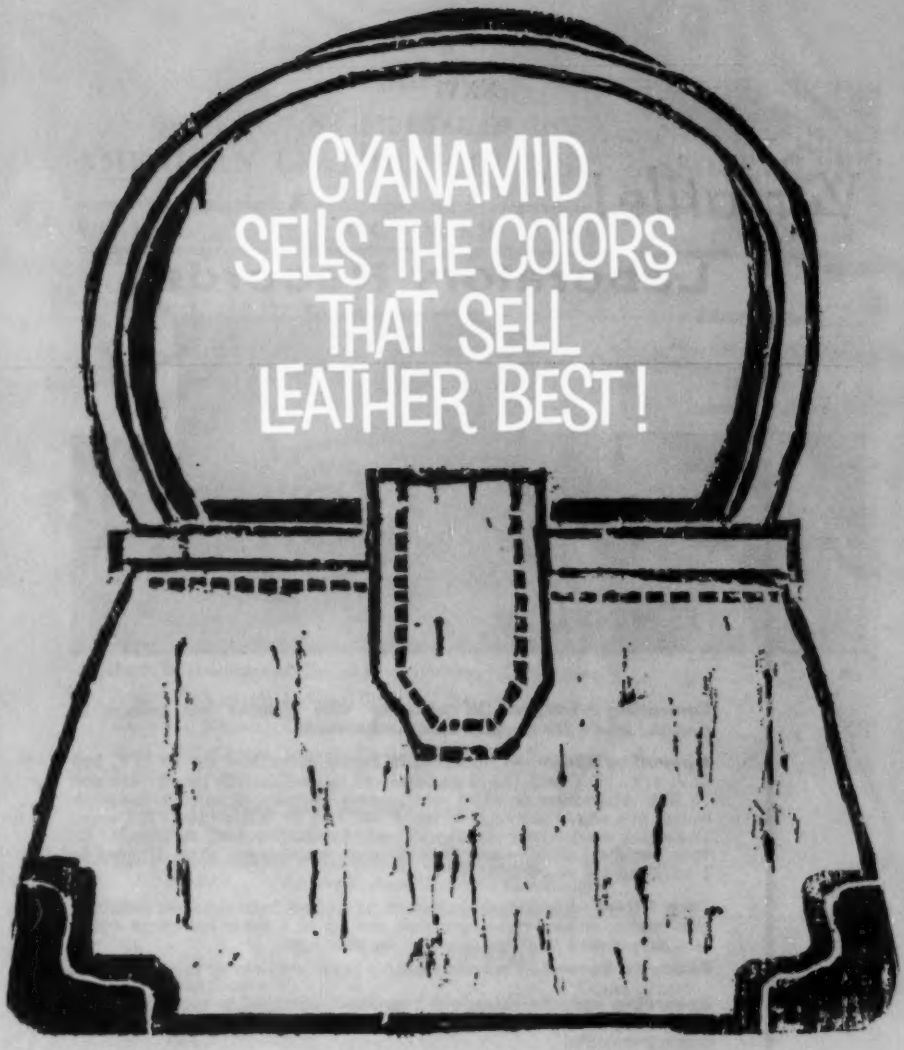
JACQUES WOLF & CO.
Chemicals

A SUBSIDIARY OF NOPCO CHEMICAL COMPANY

60 PARK PLACE, NEWARK, N. J.

Clifton, N. J. · Carlstadt, N. J. · Los Angeles, Calif.

CYANAMID SELLS THE COLORS THAT SELL LEATHER BEST!



Never before has color been so crucial in the sale of leather goods. That's why more and more leading leather producers rely on 1) Cyanamid's vast line of leather dyes... favorite building blocks of the leather color spectrum **plus** 2) Cyanamid's leather dye specialists to give intimate service, expert on-the-spot technical assistance, whenever and wherever asked. This combination of fine product and fine service has been a tradition in Cyanamid leather customer relationships for years. American Cyanamid Co., Dyes Dept., Bound Brook, N.J.

Many of the currently popular Olive Brown shades (like this one) can be formulated with this combination of Cyanamid quality leather dyes.

CALCOCID* BROWN Y

CALCOCID* BROWN 2Y

CALCOCID* BROWN RD EX.

CALCOFAST* OLIVE BROWN G

* TRADEMARK

CYANAMID

Versatile!

Laboratory Recorder

YSI MODEL 80

Operating Principle—Galvanometer with chopper bar pointer is clamped briefly for marking every two seconds.

Operating Ranges—Calibrated full scale deflections for 10 MV, 100 MV, 1 V, 10 V and 100 V and for 1 UA, 10 UA, 100 UA, 1 MA and 10 MA. Attenuator provides continuously variable adjustment between ranges and allows recording of up to 500 V or 50 Milliamperes full scale. Deflection sensitivities of from 200 microvolts per chart division to 10 volts per chart division and 20 milli-micro amperes per chart division to 1 milliamp per chart division.

Zero Offset—Continuous multiturn zero offset control allows zero left, zero center, or zero right operation and up to 4 times full chart width zero suppression in either direction on all ranges.

Ready to Record—Pressure sensitive paper requires no ink.

Recording Speeds—Standard instrument equipped to record at 1 and 15 inches per hour. Auxiliary gears available for 2, 3, 6, 10, 12 and 30 inches per hour.

Chart Characteristics—Chart width: 2.31 inches, chart divisions 50, chart length 63 feet. Readable to ±½%.

Input Characteristics—1 Megohm input resistance on all voltage ranges.

. . . . . **$295.00**

More detailed information sent upon request.

A.H.T.CO.

ARTHUR H. THOMAS COMPANY

More and more laboratories rely on Thomas / *Laboratory Apparatus and Reagents*

VINE ST. AT 3RD • PHILADELPHIA 5, PA.

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LV OCTOBER 1960 No. 10

DR. WALLACE WINDUS - - - - - - - - - - - *Editor-in-Chief*
U. S. Department of Agriculture,
Eastern Regional Research Laboratory, Philadelphia, Pennsylvania

DR. THOMAS C. THORSTENSEN - - - - - - - - *Associate Editor*
Industrial Research, P. O. Box 267, Lowell, Massachusetts

EARL J. WATT - - - - - - - - - - - - - - *Managing Editor*
Lowell Technological Institute, Lowell, Massachusetts

EDITORIAL BOARD

E. D. Compton, Eagle-Ottawa Leather Company
W. C. Henry, Ontario Research Foundation
John H. Highberger, United Shoe Machinery Corporation
Joseph R. Kanagy, National Bureau of Standards
Henry B. Merrill, 7004 Schroll Street, Lakewood, Cal.
William T. Roddy, Tanners' Council Research Laboratory
Stephen A. Shivas, John A. Lang & Sons, Ltd.
Carl G. Telander, Raser Tanning Company
Harold G. Turley, Rohm & Haas Company
Lee P. Witnauer, U. S. Department of Agriculture,
Eastern Regional Research Laboratory

ABSTRACTERS

Jose Behar B.
G. A. Bravo
Frank Bublik
James M. Cassel
Ira D. Clarke
Sverre Dahl
Clara Deasy
Raymond L. Hebert
Jerome Jansing
Liboslav Masner
G. M. Oliensis
Ralph H. Twining
J. F. Wagoner

All manuscripts should be sent to the Editor-in-Chief, 1437 Bryant Lane, Meadowbrook, Pa. Mail in reference to subscriptions, advertising, and other business should be addressed to the Secretary-Treasurer of the Association, Dr. Fred O'Flaherty, Tanners' Council Research Laboratory, University of Cincinnati, Cincinnati 21, Ohio. Checks should be made payable to the American Leather Chemists Association.

General correspondence concerning the *Journal* should be mailed to the Managing Editor. Subscriptions—$12 per year for members; $15 for nonmembers.

THE DEPOLYMERIZATION OF COLLAGEN FIBERS*

ARTHUR VEIS, JOAN ANESEY,

AND JEROME COHEN

Armour Leather Company
Chicago, Illinois

ABSTRACT

Native bovine corium collagen was partially solubilized at the shrinkage temperature. The soluble portion was fractionated by an ethanol-sodium chloride coacervation technique. The fractions were characterized by a variety of physical techniques including ultracentrifugation and light scattering. The ultracentrifuge studies clearly showed that the depolymerization of the intact fiber did not yield a gaussian weight distribution of gelatin. Several discrete molecular weight species were obtained. Since the depolymerization was carried out with minimal hydrolysis, the molecular species distributions can be related to the state of aggregation of collagen in the intact fiber. The distinction between a "collagen molecule" and the functional entity "a collagen fiber" is discussed.

—×—×—

INTRODUCTION

Recent studies have focused increasing attention on the state of aggregation of collagen molecules in intact collagen fibers (1–9). These works lead to the common conclusion that, in Jackson's words (5), "following the synthesis of the collagen molecule increasingly larger and more firmly cross-linked aggregates of these molecules are formed, requiring more and more drastic methods of extraction". The problem lies in specifying the nature of the aggregation process, and on this there is not yet general agreement.

Following Tustanovskii *et al.* (2), Banga, Balo, and Szabo (1) and Mazurov and Orekhovich (4) have concluded that while collagen fibers are physically and functionally homogeneous under physiological conditions, they are composed of two components that can be separated under other conditions.

*Presented at the Fifty-sixth Annual Meeting of A.L.C.A., Lake Placid Club, N. Y., June 21, 1960.

These components are acid-soluble "procollagen" and insoluble "metacollagen". According to these workers neither procollagen nor metacollagen fibers show the typical properties of native collagen in terms of shrinking, swelling, and electron microscopic appearance. Thus, they conclude that a complex between the two is that material which is recognized as collagen.

Jackson (5) and Gross (6) take the position that collagen fibers are chemically identical throughout and that the variations in solubility occur because of variations in the degree of organization (or crystallinity) of the basic subfibrillar molecular units (procollagen, tropocollagen, neutral-salt–soluble collagen). The more highly crystalline a part of the fiber is, the more tightly interlocked and more insoluble that part is thought to become.

Our hypothesis is that while the collagen fiber is composed of similar, basic subfibrillar molecular units, the structure is held together by occasional chemical cross-linkages that create an anisotropic but three-dimensional network that will persist even upon severe swelling or melting. As fibers mature, the average number of cross-linkages increases, but all fibers are not equally polymerized. The reason for choosing chemical cross-linking over crystallinity is based on the strength of the bonding (9).

The controlled depolymerization of collagen fiber reported here was carried out to clarify the situation with regard to the heterogeneity of the insoluble collagen structure.

EXPERIMENTS AND RESULTS

Native corium collagen

The bullhide corium collagen used in this investigation was purified by a method that differs somewhat from that we have used previously (10), and therefore, a new flow diagram is given in Fig. 1. The hide pieces were collected fresh from the kill floor and immediately washed in ice water. The major part of the hair was clipped off, and the clean strips were quickly frozen, flat, at dry-ice temperatures. The frozen strips were split into three sections with a hide splitter. The center sections were thawed in 10% NaCl solutions and represent the starting material in the flow diagram. After collection, the collagen pieces were kept at 15° or below at all times.

The major changes in procedure involved the fat removal step and the order of extraction of neutral-salt–soluble and acid-extract collagen. The freezing (11) and dehydration steps did not appear to influence the properties of the collagen, and the behavior of the two soluble fractions was normal. The amounts of materials obtained in the various extracts and residues are given in Table I.

TABLE I

YIELDS OF VARIOUS COMPONENTS FROM PURIFICATION PROCEDURES

	Weight g.	Total Weight g.	Percent Yield
Neutral-Salt-Soluble Collagen I	0.115		
" " " " II	0.822		
		0.937	0.03
Tropocollagen I	1.118		
" II	0.473		
		1.591	0.50
Intact Collagen		314.0	99.47
		316.528	

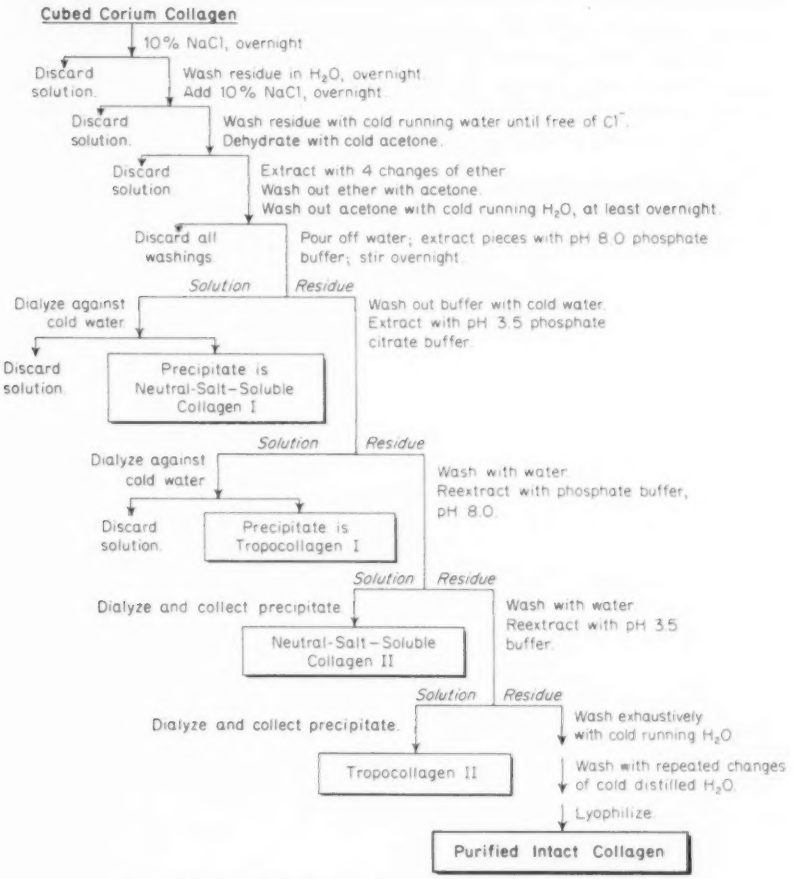


FIGURE 1.—Method for the preparation of purified collagen.

Extraction and fractionation of high-molecular-weight gelatin

We have shown (7) that intact collagen can be partially and selectively disaggregated or, in terms of the above hypothesis, depolymerized by extracting it in aqueous solutions, pH $\leq$ 7.0, at temperatures near the contraction temperature for a short period of time. The purified intact corium cubes were extracted at 60.0° ± 0.5° for one hour in an isoionic solution, pH 6.6. The procedure described by Veis and Cohen (7) was followed exactly. The water-soluble gelatin represented 8.50% of the initial collagen. Recovery was quantitative.

One-gram portions of the gelatin were fractionated by the alcohol-salt fractionation procedure (7) into six fractions of varying molecular weight. Four such fractionations were pooled to provide the gelatins for this study. The pooled results are given in Table II. The major factor in the repro-

TABLE II

FRACTIONATION OF GELATIN

Fraction Designation	Alcohol/Water Ratio	Pooled Weight Recovered (dry basis), g.	Percent in Fraction
1	2	0.2061	5.59
2	2.5	2.1832	59.19
3	3.0	0.9252	25.08
4	3.5	0.2310	6.26
5	4.0	0.0749	2.03
6	20.0	0.0681	1.85

The initial weight was 4.2244 g.; thus, the recovery was 87.3%. The losses are assumed to be about the same for each fraction so that the last column is based on percent of total recovered weight and, therefore, adds up to 100%.

ducibility of these coacervation fractionations is temperature control. The water bath was kept at 40° ± 0.05°, and the alcohol was added from a jacketed burette. The coacervates were allowed to form for ten minutes after the addition of the alcohol. Then the coacervate droplets were formed into a coherent layer by centrifugation for 10 minutes. The centrifuge head and cups were warmed to 40° with a hot-air blower and maintained that temperature during the centrifugation period. The use of several small preparative runs enabled us to keep better control over the temperature and time factors than would have been possible in a single larger-scale fractionation.

Molecular weight distributions

In addition to the information gained from the fractionation weight distributions, the gelatin in each fraction was characterized in terms of molecular

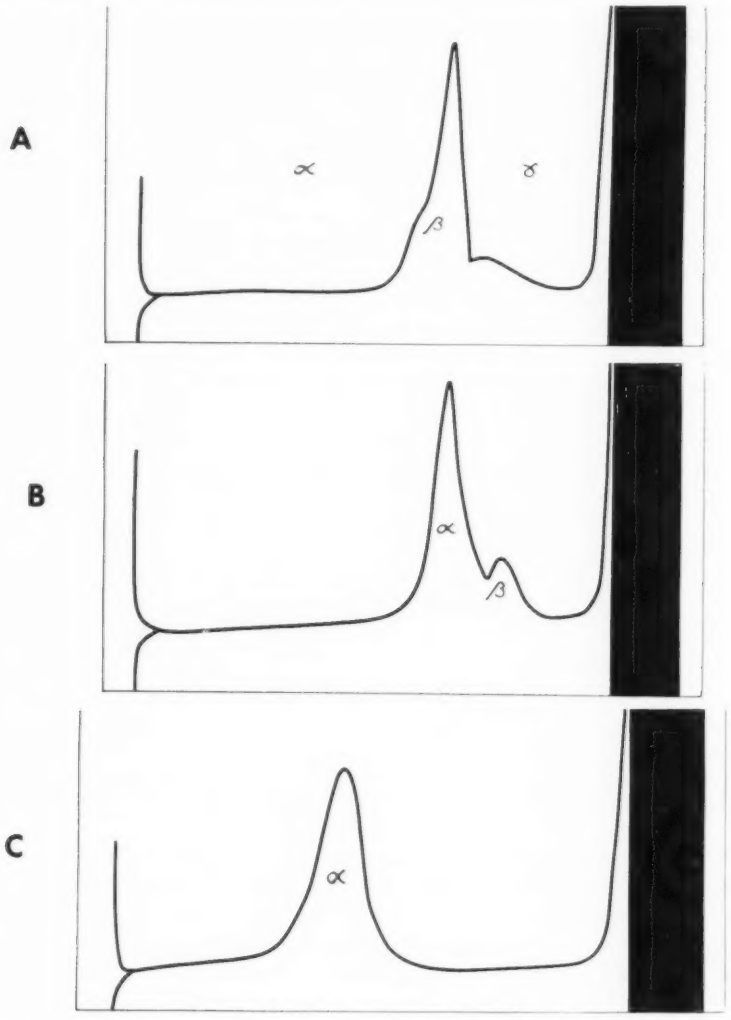


FIGURE 2.—Sedimentation diagrams for Fractions 2, 3, and 4. All analyses were carried out in 0.1*M* KCl at 40° and at 59,780 rpm. A: Fraction 2, 1.0%, 112 min. B: Fraction 3, 0.75%, 144 min. C: Fraction 4, 1.0%, 112 min.

weight, sedimentation coefficient, and viscosity. Fraction 1 was not readily soluble in water and appeared to be composed of insoluble fibrous debris suspended by the extracted gelatins. No measurements were made on Fraction 1 except to determine the amount of protein in it. The other five fractions were readily soluble in warm water (40°) or salt solutions.

Ultracentrifugal characterization.—The gelatin solutions were prepared by first soaking the dried gelatin in 0.1*N* KCl at room temperature and then warming the gel to 40°. These solutions were dialyzed overnight against 0.1*N* KCl at 4°. The solutions were subsequently warmed to 40° for at least one hour before any measurements were made. Sedimentation velocity runs were made at 59,780 rpm at a rotor temperature of 40.0°±0.1°. The Spinco Model E ultracentrifuge used was equipped with a remote temperature indicator and control (RTIC) unit. The rotor and cell were warmed to ~42° in an oven. The warm cell was then filled as rapidly as possible with the 40°-gelatin solution and inserted into the rotor. The rotor was also inserted into the centrifuge chamber as quickly as possible, and the RTIC regulating system was turned on. Because of the high rotor heat capacity only small temperature fluctuations occurred, and each solution remained close to 40° during the entire operation. The temperature was controlled at 40° during each run. The total elapsed time from the initial warming of the gelatin solution to the beginning of the centrifugation was about 1.5 hours.

Each fraction was run at several concentrations. The sedimentation coefficients were calculated for each case, and their reciprocals were extrapolated to zero concentration. In the case of Fractions 2 and 3, where more than one component was evident, the sedimentation coefficient of each was determined. The relative amounts of the various components were estimated by graphical integration of the sedimentation patterns.

Typical sedimentation photographs are shown for Fractions 2, 3, and 4 in Fig. 2. The sedimentation coefficients $S^\circ_{40,w}$ are given in Table III, which also lists the relative amounts of the various components.

TABLE III

CHARACTERIZATION PARAMETERS FOR THE EXTRACTED GELATINS, EXPERIMENTAL AND CALCULATED

Fraction	Component	$S^\circ_{40,w}$	Mw × 10^{-5}		[η]		$[\alpha]_{40}^{D}$	Fractional Composition
			(Obs.)	(Calc.)	(Obs.)	(Calc.)		
2	—		0.6		0.76		−133	
	α	4.79		1.35		0.33		0.18
	β	7.72		4.95		0.65		0.47
	γ	9.58		13.8		1.12		0.35
3	—		3.0		0.50		−127	
	α	5.00		1.35		0.33		0.46
	β	7.02		4.95		0.65		0.54
4	α	4.92	1.35		0.33		−140	—

To determine whether the presence of several discrete components was due to some reversible intermolecular interaction phenomena, sedimentation velocity experiments were carried out under a variety of conditions. Observations of the sedimentation of Fraction 2 were made in 1.0*M* KCl, 0.3*M* KCl, 0.1 μ pH 4.5 acetate buffer, 0.1 μ pH 3.0 glycine-HCl buffer, and 0.1 μ pH 9.1 glycine-NaOH (12), all at 40°. Observations were also made at 25° in hydrogen-bond-competing solvents, 6.0*M* urea and 2.0*M* KCNS, both of which have been shown to destroy gel-like aggregates in gelatin at that temperature. In every case Fraction 2 separated into the same three components in the same relative proportions as in the 0.1*N* KCl solutions. However, because of the high viscosity and density of the urea solution, the separation of the components was not so sharp as in the 2.0*M* KCNS.

Molecular weight determinations.—In spite of the evident heterogeneity of the gelatin fractions, weight-average-molecular weights were determined by light-scattering methods for Fractions 2, 3, and 4. The results are included in Table III. The analyses were carried out in 0.1*N* KCl solutions at 40°. Stock solutions of from 0.7% to 0.5% were prepared and centrifuged at 40,000 rpm in a Spinco Model L centrifuge, #40 rotor, for 1.5 hours. Half-milliliter aliquots of the centrifuged stock solution were added to 5 ml. of filtered KCl solution in the light-scattering cell. The cell was jacketed and maintained at 40° during the run. The complete scattering envelopes were recorded from 30° to 135°. The weight-average-molecular weights and Z-average dimensions were calculated from Zimm plot extrapolations. Samples of each centrifuged gelatin stock solution were taken for concentration determination, by interferometric analysis, for viscosity and for optical rotation measurements. These latter results are also included in Table III. The viscosities were determined in Ubbelohde suspended level viscometers with flow times of about 200 sec. for 0.1*N* KCl at 40°.

The stock solutions were recentrifuged at 40,000 rpm for an additional 1.5 hours, and all measurements were repeated. The data in Table III represent averages of these duplicate analyses. Other than a drop in the concentration of the stock solution, no significant variations were found on recentrifugation.

Molecular weight-molecular species relationships.—The sedimentation data clearly show that Fractions 2 and 3 are heterodisperse systems. Therefore, it is obvious that the measured molecular weights and intrinsic viscosities are average values. However, a comparison of the $S^\circ_{40,w}$ values for the various components in Fractions 2, 3, and 4 indicates that only three components, α, β, and γ, are probably present. That is, the slow component, α, has the same $S^\circ_{40,w}$ value in each of the three fractions, and β has the same sedimentation constant in Fractions 2 and 3.

By measuring the relative areas of the components in each sedimentation diagram and extrapolating these to zero total concentration, the fractional compositions ω_i of the components can be estimated. Since $(M_w)_\alpha$ and $[\eta]_\alpha$ are known from analysis of Fraction 4, these same quantities can be calculated for β and γ. For example, with $[\eta]_2$, $[\eta]_3$ and $[\eta]_4 \equiv [\eta]_\alpha$ being known from direct measurement, and with $\omega_{3\alpha}$, $\omega_{3\beta}$, $\omega_{2\alpha}$, $\omega_{2\beta}$ and $\omega_{2\gamma}$ available from the sedimentation diagrams, the equations 1, 1-A, and 1-B can be solved simultaneously to yield $[\eta]_\beta$ and $[\eta]_\gamma$.

$$[\eta]_4 = [\eta]_\alpha \tag{1}$$

$$[\eta]_3 = \omega_{3\alpha}[\eta]_\alpha + \omega_{3\beta}[\eta]_\beta \tag{1-A}$$

$$[\eta]_2 = \omega_{2\alpha}[\eta]_\alpha + \omega_{2\beta}[\eta]_\beta + \omega_{2\gamma}[\eta]_\gamma \tag{1-B}$$

Similar weight-average estimates can be made for $M_{w,\beta}$ and $M_{w,\gamma}$. The results of these calculations are in the $[\eta]_{calc.}$, $M_{w,calc.}$ and Fractional Composition columns of Table III. The essential validity of this type of calculation is verified by the fact that a plot of log $[\eta]_{calc.}$ vs. log $S^\circ_{40,w}$ is linear, Fig. 3. The over-all composition of the 60° extractable gelatin is given in Table IV.

TABLE IV

OVER-ALL COMPOSITION OF 60°, pH 6.6 EXTRACT OF STEERHIDE CORIUM COLLAGEN

Component	% Solubilized Collagen	Calculated Molecular Weight	$S^\circ_{20,w}$	$S^\circ_{40,w}$
α	27.5	1.35×10^5	3.21	4.79
β	41.3	4.4×10^5	4.57	7.72
γ	21.3	12.3×10^5	6.24	9.58

The combination of the experimentally determined light-scattering M_w average values with the experimentally determined average $[\eta]$'s also gives a straight line log-log plot following the modified Staudinger equation

$$[\eta] = 7.04 \times 10^{-4} M_w^{0.52} \tag{2}$$

The calculated α, β, and γ $[\eta]$ and M_w values fit this relationship reasonably well, Fig. 4. The $M_w - [\eta]$ relationship described by equation (2) is compared in Table V with similar relationships obtained by others for various gelatin

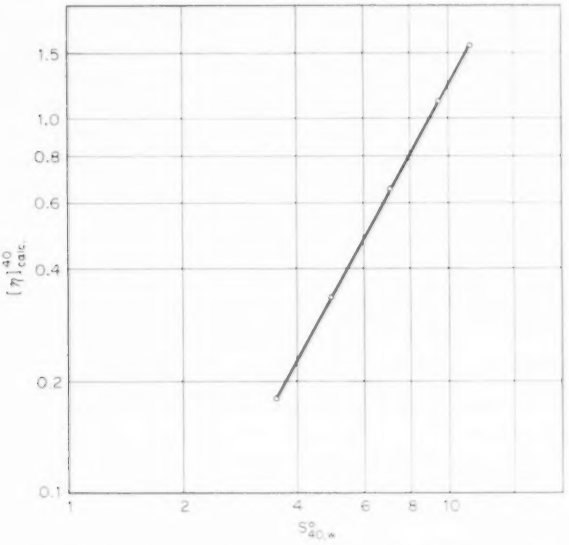


FIGURE 3.—Calculated intrinsic viscosity–sedimentation coefficient relationship for the individual components.

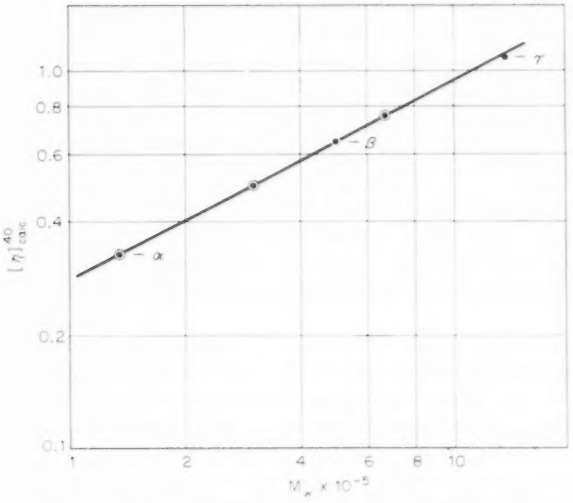


FIGURE 4.—Intrinsic viscosity–weight-average molecular weight relationships. Open circles are the experimental values for Fractions 2, 3, and 4. Solid points are the calculated values for components β and γ as obtained from equations 1, 1-A, and 1-B and from similar relationships for the molecular weight.

TABLE V

INTRINSIC VISCOSITY–MOLECULAR WEIGHT RELATIONSHIPS IN TERMS OF THE MODIFIED STAUDINGER EQUATION FOR VARIOUS GELATINS $[\eta] = KM^{a}$

Preparation	Reference	Molecular Weight Method	K	a
pH 6.6 extraction 60°	This paper	Light-scattering (weight average)	7.04×10^{-4}	0.52
Knox P-111-20 (alkali-precursor, unfractionated)	Williams *et al.* (13)	Equilibrium centrifugation (weight average)	2.9×10^{-4}	0.62
Knox B-136-1 (alkali-precursor, fractionated)	Gouinlock, Flory, and Scheraga (14)	Light-scattering (weight average)	*5.99×10^{-4}	0.55
Alkali-precursor, fractionated)	Courts and Stainsby (15)	Light-scattering (weight average)	*2.97×10^{-3}	0.45
Ossein, acid-precursor, fractionated	Courts and Stainsby (15)	Light-scattering (weight average)	*2.21×10^{-3}	0.45
Alkali-precursor	Pouradier and Venet (16)	Osmotic pressure (number average)	1.66×10^{-5}	0.885
Acid-precursor	Pouradier and Venet (16)	Osmotic pressure (number average)	1.10×10^{-5}	0.74

*Calculated from the published data. These correlations are not given in the original reports.

preparations. The wide variations make it evident that is is dangerous to make comparisons. However, each set of data is internally consistent, and this fact suggests that either there are systematic errors in some of the molecular weight determinations or that there can be wide differences in the molecular weight and molecular configuration distributions. Each of the alkali-precursor gelatins examined by Williams, Saunders, and Cicirelli (13) and Gouinlock, Flory, and Scheraga (14) sedimented as a single peak in sedimentation velocity experiments. Furthermore, systematic errors in M_w would be expected to lead to variations in K rather than in a. Thus, it is most likely that variations in the weight distributions do occur.

DISCUSSION

F. O. Schmitt (17) has summarized the current tropocollagen (TC) hypothesis of the structure of the collagen fibril. Each of the long, thin TC molecules ($\sim$2800 Å long, 16 Å diameter) contains three helically entwined

polypeptide chain helixes, and all are assumed to be essentially identical in structure and composition. However, the chains themselves are not uniform in terms of amino acid sequence. Hence, the TC molecules are polarized. Each of the several types of ordered TC aggregates is stabilized by the interactions of the side chains on adjacent TC monomer units, each aggregate representing a definite pattern of interacting side chains. In native fibrils the TC macromolecules are thought to be arranged in parallel array but are displaced in the axial direction by one quarter of a length in the adjacent macromolecules. The individual component peptide chains of the TC molecule may not be of equal length and single-chain extensions beyond the 2800 Å length may overlap to provide end-to-end bonding for the monomer units. Upon denaturation, TC separates into the three constituent peptide chains with a weight-average-molecular weight of 1.35×10^5 (18).

Within the framework of the TC monomer hypothesis there is an upper limit to the size of the denatured gelatin molecule. This upper limit is 1.35×10^5 in the straightforward interpretation or $\sim 3.5 \times 10^5$ if the 3-stranded structure is folded from a single chain.

The salient feature of this study is that the sedimentation experiments give unequivocal evidence that the gelatin obtained by the partial solubilization of collagen under mild neutral conditions cannot be represented by a Gaussian or other single-peaked molecular weight distribution function. The second major observation is that the highest weight components, β and γ, are present in substantial amounts and are clearly higher in molecular weight than the macromolecular TC monomer unit ($M_w = 3.5 \times 10^5$). Finally, it has been demonstrated that β and γ are not reduced in weight or amount by hydrogen-bond breaking reagents or by acidic or basic environments at temperatures which normally destroy gelatin aggregates.

It has never been shown that heating collagen close to its contraction temperature in neutral or slightly acidic aqueous solutions leads to anything other than denaturation (melting) and cleavage of the peptide chains. There is much evidence that such treatments increase the solubility of the collagen in dilute acids, enhance the formation of gelatin, and make the structure more susceptible to the action of proteolytic enzymes. Thus, it is reasonable to assume that the solubilization and fractionation procedures described in the preceding section were not accompanied by polymerization of the collagen structure. Consequently, polymeric units comparable to β and γ must have existed in the intact structure prior to the depolymerizing extraction. The existence of these higher-molecular-weight gelatins means that stable inter-TC linkages are formed and are probably inherent in the intact collagen fiber structure. This is the essential difference between the acid-soluble TC and the insoluble collagens.

Gustavson (19), Landucci, Pouradier, and Durante (20), Gallop, Seifter, and Meilman (21), and Mechanic and Levy (22) have each discussed the covalent interchain cross-linkages that could exist in collagenous tissue. These linkages are either ester or amide in character, e.g., interchain carboxyl-ε-lysyl peptide. For the present discussion it is not important to know their exact nature, but it is important to realize that the strength of these bonds is of the same order of magnitude as that of the ordinary peptide bond. Partial solubilization of the cross-linked structure therefore requires energies and conditions that will also hydrolyze some of the main peptide chain linkages. This energy is also sufficient to break down the cooperative hydrogen-bonded, crystalline order of the collagen fiber. The experiments of Banga (1) on the extraction of procollagen from collagen fibers were rather drastic in that the collagen was extracted in acid at 37° for several days. Still, this high temperature extraction dissolved only a small amount of procollagen. On the basis of the cross-linking hypothesis described above, the metacollagen is merely a melted, no longer anisotropic, cross-linked gel of the same chemical nature as the procollagen. The material which Banga extracts and calls procollagen is the TC which is not polymerized into the fiber structure by covalent bonds. Amino acid analyses of TC and of insoluble collagen residues from which TC has been extracted support this view, since no significant changes in amino acid composition have been noted (3, 4, 23).

The important fact that the high-molecular-weight gelatins are averaged around certain weights and are not uniformly distributed may be taken to indicate a specific rather than a random mode of polymerization. However, regardless of the mechanism of the formation of the interchain bonds, the heterogeneity of the collagen fiber is seen to reside in the heterogeneity of the cross-linkage distributions. It is not necessary to assume any heterogeneity in the basic TC monomer units, and the collagen fiber can be considered as composed of polymers of a single substance.

REFERENCES

1. J. Banga, J. Balo, and D. Szabo. *Acta Physiologica Hung.*, **9**, 61 (1956).
2. A. A. Tustanovskii, A. L. Zaides, G. V. Orlowskaya, and A. N. Mikhailov. *Doklady Akad Nauk SSSR*, **97**, 121 (1954).
3. A. L. Zaides. *Biofizika*, **1**, 279 (1956).
4. V. I. Mazurov and V. N. Orekhovich. *Biokhimiya*, **24**, 33 (1959).
5. D. S. Jackson. *Connective Tissue, Thrombosis, and Atherosclerosis* (New York: Academic Press, 1959) 67–76.
6. J. Gross. *Ibid.*, 77–95.
7. A. Veis and J. Cohen. *J. Am. Chem. Soc.*, **78**, 6238 (1956).
8. ———, J. Anesey, and J. Cohen. *Recent Adv. in Gelatine and Glue Research* (Permagon Press, 1958) 155–63.
9. ——— and J. Cohen. *J. Phys. Chem.*, **62**, 459 (1958).
10. ——— — ———. *J. Am. Chem. Soc.*, **76**, 2476 (1954).
11. J. Gross, J. Highberger, and F. O. Schmitt. *Proc. Nat. Acad. Sci.*, **41**, 1 (1955).

12. All buffers were made up according to the schemes described by G. L. Miller and R. H. Golden, *Arch. Biochem.*, **29**, 420 (1950).
13. J. W. Williams, W. M. Saunders, and J. S. Cicirelli. *J. Phys. Chem.*, **58**, 774 (1954).
14. E. V. Gouinlock, P. J. Flory, and H. A. Scheraga. *J. Polymer Sci.*, **16**, 383 (1955).
15. A. Courts and G. Stainsby. *Recent Adv. in Gelatine and Glue Research* (Pergamon Press: 1958) 100–05.
16. J. Pouradier and A. M. Venet. *J. Chim. Phys.*, **49**, 85 (1952).
17. F. O. Schmitt. *Connective Tissue, Thrombosis and Atherosclerosis*, I. H. Page, ed. (Academic Press, 1959) 43.
18. H. Boedtker and P. Doty. *J. Am. Chem. Soc.*, **78**, 4267 (1956).
19. K. H. Gustavson. *Chemistry and Reactivity of Collagen* (New York: Academic Press, Inc., 1950).
20. J. M. Landucci, J. Pouradier, and M. Durante. *Recent Advances in Gelatine and Glue Research* (Pergamon Press, 1958) 62–67.
21. P. M. Gallop, S. Seifter, and E. Meilman. *Nature*, **183**, 1659 (1959).
22. G. L. Mechanic and M. Levy. *J. Am. Chem. Soc.*, **81**, 1889 (1959).
23. J. H. Bowes, R. G. Elliott, and J. A. Moss. *Nature and Structure of Collagen* (Academic Press, 1953) 199–207.

Received June 29, 1960.

DISCUSSION

DR. PETER BUECHLER: Dr. Veis and his colleagues have again added to our rapidly growing knowledge of collagen structure. In this paper, Dr. Veis has adduced evidence to support the hypothesis which he has been advocating for several years—viz, that cross-linking is an important part of the collagen structure and is responsible for many of its properties. From the viewpoint of the tanner, this would be a very desirable condition.

In recent years two types of replacement for leather have been receiving very considerable attention in research. In one of these, attempts have been made to replace leather with an all-synthetic product. A successful competitor for leather of this nature could make serious inroads on shoe upper leather sales. However, as the sales of leather for this purpose went down, hide prices would drop, because hides are a by-product of the meat industry and have to be utilized. Drops in hide prices would then make leather more competitive in other fields where it is suffering from price disadvantages, fields such as upholstery, bag, case and strap, bookbinding, etc.

It would also reduce the price of shoe upper leather until it is again competitive. Thus just as many hides would be tanned and the wise tanner who watched the markets would still be in business.

However, the second class of replacement which has been receiving research attention is much more dangerous to the tanner. I refer to the work

on leathers made from reconstituted collagen. The danger from materials of this type is that potentially they can compete with the tanner for his raw material and thus keep the prices of raw stock at a high level.

Here we come to the practical importance of Dr. Veis's paper. If the solubilization process disrupts cross-links, it makes reconstitution more difficult. As one who has had the job of cross-linking long chain molecules, I assure you that it is a process difficult to control. At an exact proportion of cross-links, very desirable properties can be obtained. However, very little less cross-linking can lead to too little strength and too much solvent susceptibility. Very little more cross-linking can lead to an embrittlement and lack of flexibility of the product. If Dr. Veis is correct in his hypothesis concerning cross-links in collagen, it greatly adds to the technical difficulties of making leather substitutes from reconstituted collagen.

With regard to the paper itself, I should like to ask Dr. Veis two questions. One of them is whether or not he has taken into account sufficiently the Johnston-Ogston effect whereby one sedimenting fraction affects the rate of sedimentation of another sedimenting fraction? I think this is quite important because the calculation of molecular weights made by Dr. Veis and his colleagues depends very much on the weight fraction as determined from the sedimentation rate.

DR. VEIS: The Johnston-Ogston effect is important and has been taken into consideration. This effect, in a two-component system for example, leads to an apparent accumulation of faster sedimenting material in the slower component boundary and false values for the fractional composition. This error is larger, the closer the S values are together. Therefore, as indicated in the paper without elaboration, we had to extrapolate the apparent composition data to infinite dilution. The fractional composition data in Tables III and IV were obtained in this way and may have been surprising to one who casually examined the sedimentation diagrams of Figure 3.

The separation of the mixtures into several components is not affected by the Johnson-Ogston effect, and the fact that one finds several apparent components means that there are indeed several components or that some reversible aggregation is occurring.

DR. BUECHLER: How has it affected the molecular weight?

DR. VEIS: The molecular weights as calculated here were not determined from the sedimentation experiments. If we had the pure components we could have measured the sedimentation coefficient and diffusion constants and gotten molecular weights, but we had to go to the light scattering method to calculate the average molecular weights.

DR. BUECHLER: Another question I would like to ask here is: Boedtker and Doty have shown that aggregation of gelatin molecules occurs in a critical temperature range which in 0.15 molar citrate is 20-36 degrees Centigrade. Is it possible that in raising the temperature from your dialysis temperature of 4 degrees in 0.1*N* KCl to 40 degrees prior to ultracentrifugation, you may have also passed through such a critical temperature range and thus caused aggregation to the high-molecular-weight fraction which you have found?

DR. VEIS: In the experiments we did and in the gelatin we used, we were always careful to keep this particular problem in mind. So the solutions were kept, after the gelatin solutions had formed or before measuring them, at 40° for an hour or more. Even in the sedimentation experiments the cells were filled and kept in rotor at the equilibrium for an hour and a half before the rotor was started.

There have been many experiments by Boedtker and Doty and by ourselves, which showed that the aggregation phenomenon in these solutions was negligible at 40 degrees. One hour of heating thoroughly erases the thermal history of a gelatin solution.

I should point out too that we measured also optical rotations for these gelatins at various points in the process and they were always around minus 130, at 40 degrees in 0.1*N* KCl.

DR. BUECHLER: I think the recent work referred to by Dr. Highberger in which he spoke of the effect of trypsin on tyrosine linkages in some way may be contributory to the belief in a cross-linking mechanism. Would you care to comment, Dr. Highberger?

DR. HIGHBERGER: The type of linkage I was discussing this morning was not cross-linking. We have confined our attention primarily to the end-to-end linkage. I have no doubt that a cross-linking such as Dr. Veis described certainly must exist. There must be some explanation for the difference in solubility between the portions of collagen in a given tissue, and this seems a logical explanation of it and his evidence seems very convincing.

I would like to ask one question: Do you consider the component that you named alpha to be identical with the ordinarily taken alpha?

DR. VEIS: Yes, the sedimentation coefficient in S_{20} terms comes out to be the same as the alpha component of Doty and Boedtker.

DR. HIGHBERGER: Then why isn't there a corresponding beta component?

DR. VEIS: That is a very good question. I am not sure but that the conditions under which we did the extraction had something to do with it. We raised the temperature, if you recall, in obtaining these gelatins, to 60 degrees. And if you take a parent gelatin and heat it under similar conditions then you only have alpha components. You don't maintain beta under those conditions.

One should really have called these, I suppose, beta prime and gamma, rather than using the beta designation.

MR. CASSEL: Dr. Veis, I gather from your approach that it should be impossible to get a high yield of soluble collagen from cowhide by extracting at low temperatures for a long enough time. Now, I am aware of some work along this line that Dr. Kroner was doing at the United Shoe Machinery Corporation, where I believe he had extracted up to 10 per cent of the collagen by continuing to extract at low temperature.

The question is, IF they had kept on doing it and still refrained from destroying the collagen by bacteria or other means, would they have been able to continue to extract?

DR. VEIS: It is possible, but you have an additional factor, and that is that you are considering extremely long time intervals. On a diffusion basis, if the collagen structure were all uniform, then you would expect that the rate at which the solubilization occurred at low temperatures in acid, from an intact collagen fiber, would have remained constant or actually increased. Because as you dissolve material from the fiber, the surface area of the fiber relative to its weight increases, and the spaces between the fibers have to increase, so that you might expect faster diffusion rate with time.

Actually, I think you will find it gets slower and slower. You can carry out a hydrolysis of ester linkages or other covalent bonds in weeks and months at rates that you would not ordinarily notice at all, in the usual kind of solubilization experiment. So that it is possible that you could carry out a hydrolysis because you have the local concentration effect. The concentrations of the reactants are very large within the fiber. And the rates of hydrolysis could be very, very slow.

THE TEMPERATURE DEPENDENCE OF THE BREAKING OF HYDROGEN BONDS OF COLLAGEN BY UREA AND SOME OF ITS IMPLICATIONS

K. H. GUSTAVSON

Garverinäringens Forskningsinstitut
Stockholm, Sweden

ABSTRACT

The solubilization of hide collagen by concentrated solutions of urea (4–8*M*) is highly temperature-dependent. These solutions do not degrade collagen appreciably at temperatures less than 30° C. At temperatures above 30°–35° C., marked destruction of the skin structure by urea is suddenly induced. The chemical alterations of the protein which are produced by the treatment are evaluated by data from (*a*) the fixation of cationic chromium complexes, specifically reacting with the carboxyl ions of collagen as a measure of changes in these groups, and (*b*) the affinity of the treated specimens for extremely basic chromium chlorides and sulfitochromiates for indicating any changes in the reactivity of nonionic protein groups, primarily the hydrogen bonding on the keto-imide groups. The data prove the rupture of the hydrogen bond bridges on the last-mentioned groups to be the dominating reaction in the interaction of the resonating molecule of urea with collagen in 4–8*M* solution at 37° C. Another most effective hydrogen bond breaker of collagen, sodium perchlorate, is highly dependent on concentration. Thus, solutions weaker than 2*M* attack collagen only slightly at room temperature. Destruction of the protein sets in most suddenly on treatment with solutions of 2*M* strength or greater, which causes losses of collagen of the order of 30–80% within a few days. The bearings of the findings on the temperature dependency of the hydrogen-bonding interactions on the concepts of the mechanisms of the major tannages are outlined.

—×—×—

INTRODUCTION

It has been pointed out in various connections (1) that urea, which in concentrated solution is an effective breaker of hydrogen bonds of globular proteins (2), has hardly any permanent effect on bovine collagen at room

temperature (20° C.) in 4–8*M* solutions, even upon prolonged treatment, as far as irreversible alterations are concerned. Its hydrogen-bond-breaking power first sets in at temperatures exceeding 30° C., resulting in permanent changes of the protein. At temperatures of 37°–40° C. drastic destruction of collagen is obtained in 24–48 hours in 4–8*M* solutions, 50–80% of the collagen being solubilized (1). During such brief treatment in water of 37°–40° C., only a slight denaturation or reversible "incipient shrinkage" of isoelectric collagen in the form of calfskin pelt occurs, which indicates that heat itself (hydrothermal denaturation) is not responsible for the drastic change in solubilization and properties of the collagen obtained in urea solution on the relatively small temperature increase. On the other hand, the combined effect of heat and the weak electrostatic forces, which underlie the bond-breaking power of the urea molecule in its resonating state, seems to be necessary for the degradation of the skin protein and for setting free reactive groups. Urea was selected as the reagent for the dislocation of hydrogen bonds in preference to the ionic type of agents with that function, since it is a nonionic compound, its molecule possessing electrostatic forces by virtue of resonance (3, 4). Urea systems of globular proteins are usually made 6.6*M* (2). The shrinkage of collagen by strong urea solutions was reported by Katz and Weidinger as far back as 1933 (5).

The denaturation and solubilization of collagen by urea is not only a function of temperature; to a very high degree the concentration factor enters. The lower limit is about 2*M*. The effect of the concentration is still more conspicuous on treating collagen by sodium perchlorate. At a concentration of 2*M*, the destructive action suddenly sets in (6). Chvapil (7), not aware of the preliminary data communicated in the monograph (6), has found that for the instantaneous shrinkage of rat tail tendon to occur, the concentration of the perchlorate must be at least 2*M*. An interesting feature is that mucoproteins are released during the contraction of the fibers, and small proline-hydroxyproline polypeptides during the following relaxation. Perchlorate solutions of 1.9*M* strength had no effect. This interesting neutral salt effect will be the subject of a forthcoming paper.

The temperature dependence is not so apparent for many other well-known hydrogen bond breakers. Certain strong electrolytes are very effective even at about 20° C. in concentrated solution (8). However, the strong charges of the electrolytes introduce undesired complications. A rather complete list of some 80 hydrogen-bond-breaking agents, classified according to their effectiveness of liquefying swollen gelatin at various molarities, has been published by Courts (9), based on his own investigations.

In the present paper some selected data which have been obtained in an extensive series of investigations will be presented to illustrate the effect of urea pretreatment of collagen upon its reactivity toward some selective agents, mainly different types of chromium complexes. Further, the effect

of prolonged contact of collagen with water in the range 20°–40° C. is included. Apart from the fact that such tests are requisite as blanks for the corresponding urea experiments, the alteration of skin collagen which is induced by water at a temperature far below the established critical temperature of instantaneous shrinkage is of theoretical, and even practical, interest.

Another main object of this paper is to demonstrate how the findings as to hydrogen bond breaking in the collagen structure by urea bear on the conception of the mechanism of the major tanning processes.

EXPERIMENTAL AND MATERIALS

The behavior of collagen to urea solutions at temperatures of 20° and 37° C. was studied. The substrate was delimed isoelectric calfskin pelt (ash <0.1%) with the grain and flesh layers split off. Strips of the lightly pressed pelt, 40 x 10 mm., weighing 100 g. (= 35.0 g. of collagen), were treated in 400-ml. portions of the solutions (covered with toluene) which are

TABLE I

EFFECT OF UREA TREATMENT AT 20° C. ON COLLAGEN (PELT)

	Conc. of urea, in mole/l.						
	0	1	2	3	4	6	8
% loss of collagen	<1	<1	<1	1	2	3	5
Ts in °C.	65	65	64	64	63	63	62
Uptake of 0.1N HCl, in ml/g collagen	9.2	9.2	9.1	9.2	9.1	9.2	9.2

listed in Table I for 14 days at 20° C. The shrinkage temperature of the thoroughly washed stock was determined, as well as its weight after light pressing and the contents of dry substance and collagen. The latter determinations served as a control on the determination of solubilized collagen from the analysis of the residual urea solutions, by which solubilized collagen was obtained as the small difference between two large figures, i.e., (dissolved collagen + urea) − original urea. Table I shows the pertinent data.

The alterations in functional groups of the collagen were ascertained by estimation of its binding power for compounds reacting specifically with one or the other of the two principal types of collagen groups: (*a*) ionic groups, primarily the carboxyl ions and secondarily other electropositive protein groups, and (*b*) nonionic groups, mainly keto-imide groups of collagen. As reagents for the reaction of the carboxyl ions, equilibrated solutions of

basic chromium sulfate (10) and chloride (11) were selected, denoted by No. I and No. II respectively. The chromium complexes of these solutions carried positive charges (12). Their fixation by collagen is generally conceived to be specifically on the anionic carboxyl groups. The keto-imide groups are not involved. The reactivity of the basic protein groups was determined by the degree of removal of hydrochloric acid by the collagen from 0.1*N* HCl solution, 1*M* in respect to NaCl, treating 1.0 g. of collagen with 25.0 ml. of 0.1*N* HCl solution for 2 hours. The effect of the urea treatment on hydrogen-bonding potency of the nonionic protein groups, mainly the –CO·NH– links, was ascertained by determination of the amount of vegetable tannins (wattle extract) irreversibly fixed by collagen on treatment of 1.0 g. of collagen in 1, 2, and 5% tannin solutions, gradually increased, for 144 hours. Further, solutions of extremely basic chromium chloride, 33% acid (No. III) (12) and highly aggregated sulfitochromiate (No. IV) (13) served for assessing the keto-imide groups available for hydrogen bonding and binding of the nonionic chromium compounds.

The following solutions of equilibrated basic chromium salts, containing 1.0 equivalent Cr per liter, all cationic, were employed: I. 67%—acid chromium sulfate, made by reducing a solution of sodium bichromate by sulfur dioxide. Its composition corresponded to the empirical formula: $Cr_2(OH)_2(SO_4)_2 \cdot Na_2SO_4$. II. 67%—acid chromium chloride of composition corresponding to the empirical formula: $Cr_2(OH)_2Cl_4 \cdot 2NaCl$. It was prepared by adding one mole of NaOH to one mole of $CrCl_3 \cdot 6H_2O$.

The affinity for collagen of the following two chromium compounds, measured by the amount of chromium combining with the hide protein, is taken to approximate the amount of reactive keto-imide groups, i.e., those in the uncompensated state: III. 33%—acid chromium chloride of composition corresponding to the empirical formula: $Cr_2(OH)_4Cl_2 \cdot 2NaCl$. This solution was obtained from a solution of the 67%-acid chromium chloride, free of neutral salts, by the addition of one mole of sodium hydroxide per mole of chromium. It contained 32% cationic and 68% uncharged chromium complexes (12). IV. A solution of sodium—sulfito—sulfato—chromiate was made by adding 2.5 moles of sodium sulfite per mole of Cr_2O_3 to a solution of *salt-free*, 67%-acid chromium sulfate (13). The resulting solution, which was prepared immediately before use, in contrast to the equilibrated solutions of the preceding types, contained mainly uncharged and negatively charged chromium complexes of considerably higher degree of aggregation than the complexes present in the other three solutions (13).

Portions of pelt equal to 1 g. of collagen were treated for 144 hours with 25-ml. portions of these solutions of an initial concentration of 1.0 equiv. of Cr (25.3 g. Cr_2O_3) per liter. The results obtained in the urea treatment series, performed at about 20° C., are collected in Table II, which also includes the data for the vegetable tannin fixation (wattle extract) by the

TABLE II

EFFECT OF UREA PRETREATMENT AT 20° C. ON THE REACTIVITY OF COLLAGEN

	Conc. of urea, in mole/l.						
	0	1	2	4	3	6	8
% Cr_2O_3 fixed by collagen from							
I	9.2	9.1	9.1	9.2	9.2	9.4	9.4
II	7.0	7.2	7.1	7.2	7.3	7.4	7.6
III	10.3	10.1	10.2	10.3	10.4	10.6	10.6
IV	11.8	11.6	11.8	11.9	12.0	12.2	12.4
% tannin fixed on collagen basis (wattle extract)	38	37	38	38	37	38	39

various collagen specimens. The values for tannin fixation pertain to the irreversibly bound compounds of the vegetable tanning extract. The marked effect of hydrothermal denaturation of collagen on the fixation of vegetable tannins has been demonstrated (1, 14), as well as the same effect by pretreatment of collagen with concentrated solutions of lyotropic neutral salts (15).

Table I shows that hardly any collagen was solubilized on treatment with urea at concentrations up to 4*M* at room temperature for 14 days. Only small amounts of collagen were lost to the 4–8*M* solutions. Marked swelling and shrinkage of the pelt treated in the solutions of urea at concentrations greater than 4*M* occurred, but by removal of the urea by prolonged washing, the swollen and shrunk pelt was brought practically to the original state of water-holding (1). Only slight changes of the shrinkage temperature of the treated skin specimens after the removal of the urea were recorded. Further, the acid-binding capacity of the urea-treated specimens did not differ from that of the untreated skin, indicating that the reactivity of the basic protein groups was not changed.

The irreversible fixation of the chromium complexes applied, and of the vegetable tannins, was practically independent of the pretreatment. The data from series No. I and No. II prove that the urea pretreatment at room temperature has no appreciable effect on the reactivity of the carboxylic groups. Neither are the nonionic protein groups, primarily the –CO•NH– links, involved, as indicated by the chrome fixation by the various skin specimens from solutions No. III and No. IV, as well as by the results from the wattle series.

TABLE III

EFFECT OF UREA PRETREATMENT AT 37°C. ON COLLAGEN (PELT)

	Conc. of urea, in mole/l.			
	0	2	4	8
% loss of collagen	2	~40	~80	~70
Ts in °C.	62	~45	~35(gel)	<40
Uptake of 0.1N HCl, in ml/g collagen	9.2	~ 9.5	—	~9.5

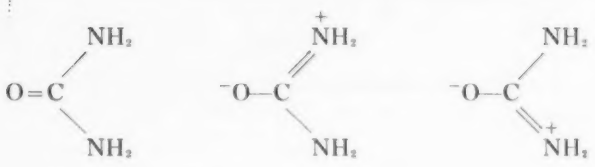
TABLE IV

EFFECT OF UREA PRETREATMENT AT 37°C. ON THE REACTIVITY OF COLLAGEN

	Conc. of urea, in mole/l.			
	0	2	4	8
% C_2-O_3 fixed by collagen from				
I	9.4	9.8	10.7	10.3
II	7.6	8.2	~10	9.1
III	11.0	15.7	~30	~28
IV	16.1	23.6	~55	~44
% tannin fixed, on collagen basis, from wattle extract	40	~45	—	~70

DISCUSSION

It seems justifiable to conclude that prolonged treatment of skin collagen in concentrated solutions of urea at temperatures about 20° C. causes some reversible alterations, affecting the water-retaining property and the hydrothermal stability, which is slightly lowered. This reversibility appears to be a consequence of the interaction of the urea molecule by resonance (3, 4). Thereby, weak polar forces are induced which enter into electrostatic interaction with weakly polar groups of the protein, such as the –CO·NH– links, which are in resonance also. The states of the urea molecules in solution are represented by the following structures (3, 4):



The thermochemical value of the resonance energy of urea is 37 kcal/mole. From the value of the interatomic distances, it is estimated that 20% of each of the C - N bonds have double-bond character, leaving 60% for the C - O bond (4).

In Table III, data from the corresponding series of treatments at 37° C. for 72 hours are shown.

Temperature Factor

When one considers the data in Table III, the destructive action of the 4 and 8*M* solutions of urea is particularly conspicuous. By a temperature increase of about 10° C. a drastic change in the reaction between urea and collagen takes place, with gelatinization of the skin, and practically complete destruction in some instances, even in the relatively short period of 48–72 hours (1). The figures for the fixation of chromium in Table IV indicate a slightly increased binding of the cationic chromium complexes (No. I and No. II), showing that the degradation of collagen has produced a small, but definite, increase of reactive carboxyl groups. Since the acid-binding capacity is augmented to a minor extent also, the cleavage of some –CO·NH– groups is indicated. However, an opening-up of ring structures formed by condensation of the glutamic acid residue, involving the γ-carboxyl, as envisaged by Huggins (16), is also possible. The result would be the release of carboxyl groups not previously available to the chromium complexes.

Great importance should be attached to the data for the chrome fixation from solutions No. III and No. IV. Solution No. III, which contains mainly noncationic chromium complexes, shows marked affinity for polyamides (17) whose principal reaction sites are the regularly occurring –CO·NH– group (18), by which they bind vegetable tannins irreversibly, probably by means of hydrogen bonding of the phenolic hydrogen atom on the keto-amide group. The oxygen atom of the carbonyl groups is believed to function as an acceptor (19). Since only the keto-imide group is involved in this polyamide fixation, the view that the main part of the noncationic chromium complexes of the extremely basic chloride is bound to collagen by coordination on these groups appears to be justified (20). The latter groups are internally compensated in the native collagen by hydrogen bond bridging. The interaction of collagen with urea in concentrated solution would then logically be conceived as a competition of the resonating form of urea with this main type of hydrogen

bonds of collagen: $\diagdown\!\!\diagup$CO←HN$\diagdown\!\!\diagup$, for the possession of the keto group. This freeing of the adjacent keto-imide groups from their internal compensation, resulting from the successful competition of the urea molecules, leads to swelling, mainly permanent. At temperatures >30°–35° C., this swelling is irreversible, probably in consequence of the unfavorable steric conditions produced. The distance between the original hydrogen bond sites in the native protein has probably been enlarged to an extent preventing the reformation of the cross-linkage. Hence, a number of new sites of reaction should be made available to the nonionic chromium complexes and the vegetable tannins. Moreover, the cohesion of the trihelical units is severely impaired. With the concomitant cleavage of some weak keto-imide links, shorter protein chains presumably are formed. The final result of this radical impairment of the strength of the structure is solubilization, whereby predominantly high-molecular products (progelatins) are formed. The blanks, i.e., the pelt kept in water at 37° C. for the same length of time as the urea specimens, show only a slightly lower degree of stability than the original pelt, as the figures for solubilized protein and shrinkage temperature bring out. Hence, the conclusion seems justified that this most far-reaching action of urea at temperatures exceeding 35° C. is caused by the urea and is not a hydrothermal effect, although heat has to be supplied for activation of the urea molecule for the breaking of the hydrogen bonds. The effect of the hydrothermal denaturation of collagen (shrinkage) on its binding capacity for vegetable tannins and neutral or negatively charged chromium complexes is very much the same as that of urea (21). Moreover, the fixation of cationic chromium complexes by collagen is not influenced by the shrinkage of collagen (1, 14). It is generally conceded that breaking of cross-linkages of the hydrogen bond type is the principal reaction occurring in hydrothermal shrinkage.

The influence of the temperature of the urea-collagen system on the activity of the functional groups which are the sites of binding of the noncationic chromium complexes is strikingly illustrated in Fig. 1. Curve *U* represents the chrome fixation from the 33%-acid chromium chloride (solution No. III) by specimens of pelt which have been treated in 4*M* urea for 96 hours at 10°, 20°, 30°, and 37° C. The curve marked H_2O shows the effect on the chrome uptake of keeping the pelt in water at these temperatures. The abrupt rise of the curve of chrome fixation for the specimens treated with urea at temperatures exceeding 30° C. is very evident, whereas the amounts of chromium fixed by the water-treated pelt are practically independent of the temperature. This 200% increase in fixation for a temperature increase of only a few degrees is typical of reactions of hide proteins with hydrogen-bond-breaking agents.

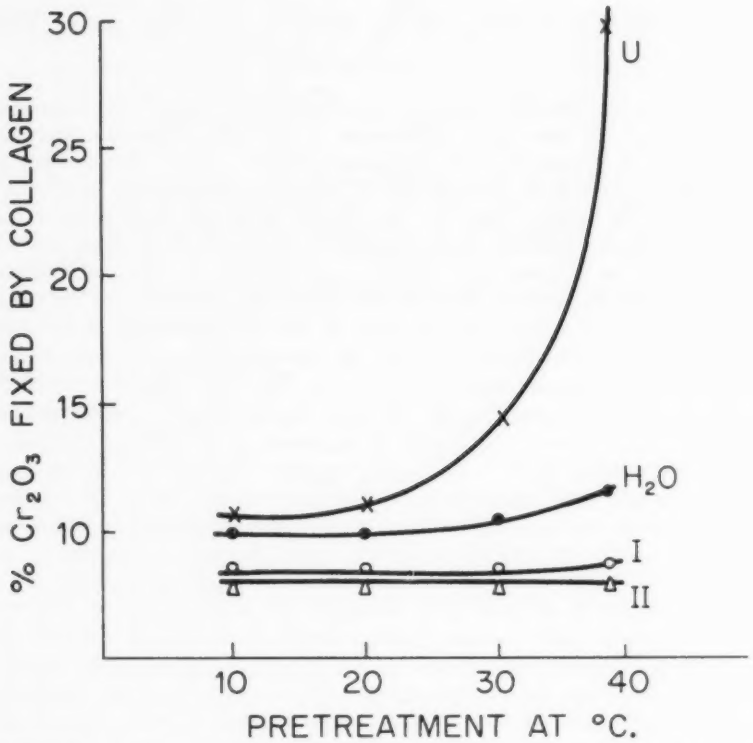


FIGURE 1.—Chrome fixation by collagen which has been pretreated in a 4*M* solution of urea and in water at temperatures of 10°, 20°, 30°, and 37° C.

U: Urea-treated pelt, tanned by 33% -acid chromium chloride, 1 eq/l Cr.

H_2O: Blank in water, tanned by 33% -acid chromium chloride, 1 eq/l Cr.

I: Urea-treated pelt, tanned by 67% -acid chromium sulfate, 1 eq/l Cr.

II: Blank in water, tanned by 67% -acid chromium sulfate, 1 eq/l Cr.

The corresponding curves I and II, depicting the fixation of cationic chromium complexes by the carboxyl ions of collagen from the 67% -acid chromium sulfate (solution No. I), show that this reaction is practically independent of the temperature of pretreatment of the collagen, indicating that ionic valency forces of collagen do not, on the whole, participate in its denaturation (14, 15).

It should be noted that treatment of pelt in water of 45°–50° C. for a few days results in incipient shrinkage which is permanent. Such stock possesses

markedly greater affinity than the original pelt for the noncationic chromium complexes employed in this investigation (20, 21). The curves in Fig. 1 bring out the fact, again to be emphasized, that a certain measure of kinetic energy is required to induce the reaction of urea by releasing the compensation on the keto-imide groups by hydrogen bonds.

Concentration Factor

The abrupt change of the normal urea molecule to an activated state within a temperature interval of a few degrees is characteristic of uncharged molecules exerting electrostatic effects by resonance on proteins. The concentration of the solution used for pretreatment of collagen exhibits a similar sharp rise of reactivity. Urea is not the best substance in that respect, although its dissociating power on globular proteins is confined to solutions of molarities exceeding four. In the pioneer experiments 6.6*M* solution was generally employed (2). An excellent example of a compound with an exceedingly great concentration dependency is sodium perchlorate (7), and also to a lesser degree the less soluble sodium periodate in the pH range 5–7 (22). Its action as an oxidant is not evident in neutral solution at room temperature. Sodium perchlorate, a strong electrolyte, is a most potent hydrogen bond breaker, as are neutral salts of greatly differing size of cation and anion generally, even at room temperature (22, 23). The change of the water equilibrium, and the "icelike" water of the proteins, is likely the governing factor in this neutral salt effect. Instead of showing a temperature effect, the action of the sodium perchlorate on collagen is exceedingly strongly concentration-dependent. It has very little solubilizing power on collagen at concentration less than 2*M*. Then, at this critical point, the labilization and solubilization sets in, increasing the loss of collagen from a few percent to amounts of the

TABLE V

THE CONCENTRATION FACTOR IN THE ACTION OF SODIUM PERCHLORATE ON COLLAGEN (20° C.)

No.	Molarity of $NaClO_4$	% Loss of Collagen	% Cr_2O_3 Fixed by Collagen from	
			I	IV
1	0	0.2	9.2	17.8
2	0.25	0.5	9.1	18.0
3	0.5	0.8	9.2	17.7
4	1.0	1.7	9.3	18.1
5	1.5	5.2	9.3	20.4
6	2.0	~67	9.8	~33
7	3.0	~71	10.4	~40
8	4.0	~60	11.0	~48

order of 30–70% in a few days at room temperature. The data in Table V exemplify the concentration dependency. Specimens of splits of light cowhide were treated for 7 days in solutions of increasing concentration of sodium perchlorate at room temperature. The treated pelt was washed free from the salt and treated with cationic chromium complexes (solution No. I) and the noncationic sulfitochromiate complexes (solution No. IV) for 72 hours, for assessing the changes in ionic and nonionic protein groups respectively. Table 19 in ref. (6) is noted in this connection.

This large effect obtained by increasing the concentration of sodium perchlorate from 1.5 to 2.0*M* is unique as far as the neutral salt effect is concerned. A gradual increase is commonly shown, with maximal action on collagen in 1–2*M* calcium chloride, and 2*M* sodium iodide (8). However, sodium perchlorate shows no concentration maximum in its solubilization of collagen. It has already been mentioned that, in unpublished work, Chvapil and coworkers (7) have independently obtained a still sharper concentration effect, since they report that 1.9*M* sodium perchlorate has no action on collagen fibers, whereas 2.0*M* induces marked shrinkage at room temperature (7).

In recent researches by Harrington and Schellman (63) it is inferred that the action of dispersing neutral salts, particularly concentrated solutions of lithium bromide, on proteins differs from that of the ordinary organic compounds of hydrogen bond breakers. By the latter agents intermolecular (interhelical) hydrogen bonds are ruptured mainly. The "lyotropic" neutral salts have in common the property of enormous activity coefficients in concentrated solutions. This means that the thermodynamic activity of the solvent (water) in these solutions is greatly reduced. Hence, they tend to transform the fibrous structure of the protein, which is dependent on the presence of *interhelical* hydrogen bonds, into helical structures containing the maximum number of *intrahelical* and intramolecular hydrogen bonds. This implies greater stability of the helices. This concept is based on the behavior of α-helices, such as silk-fibroin, in solution. However, the possible shift of the strength of the inter- and intrahelical hydrogen bonds in collagen by the action of such neutral salts seems worthy of notation, apart from the water-equilibrium (breaking of hydrogen bonds in "icelike" water), as suggested by Klotz (64). It is recognized that the effect of the "lyotropic" neutral salts on collagen is in some respects *opposite* to that of the normal hydrogen-bond-breaking agents, such as saturated solutions of urea, guanidinium salts and formamide. For collagen, however, the *trans-cis* isomerization of the proline-hydroxyproline bonds (as in the gly - pro - hypro sequence) will likely prove to be a governing factor (65).

SOME IMPLICATIONS ON THE MECHANISM OF TANNAGES

The temperature function discussed has also some bearings upon the problem of the mechanism of tannages. This has already been exemplified

in what has long been known, viz., the hydrogen bonding of polyphenols (tannins) by collagen and also the uptake of nonionic chromium compounds by nonionic reaction sites. Among the other major tanning processes the common cationic type of chrome tannage holds a position of its own, to be discussed later. The fixation of formaldehyde by collagen is independent of the state of hydrogen bonding of collagen, and hence of pretreatment with urea and of heat denaturation (24). This is not unexpected, since the reaction of formaldehyde with collagen, as usually carried out, is restricted to the basic protein groups (25–27), as is also the quinone tannage (28). In view of these differences, it is of interest to look into the problem of the temperature dependence of these tannages.

Vegetable tannage.—Since, as shown in the foregoing, the hydrogen-bonding mechanism of urea on collagen is greatly facilitated at temperatures exceeding 30° C., it would be expected that the interaction of similar weakly polar compounds, for instance, polyphenols, with collagen should be favored by rise in temperature from 20°–25° C. to 35°–40° C. This is actually the case, as the pioneering investigations of Thomas and his coworkers clearly demonstrated (29). Hide powder was the substrate, which for this special purpose is preferable to intact skin because the complication of the temperature effect on the diffusion of the solute into the substrate is largely eliminated. By increasing the temperature of the tanning bath from 25° to 37.5° C., the rate of the irreversible fixation of wattle tannins was increased by 100–300%, depending on time, concentration, and pH value of the solution. Under conditions approaching equilibrium the augmentation was about 100%. The degree of augmentation of the binding of the various tannins differs considerably according to their nature and the experimental conditions. Moreover, it should be noted that, apart from the binding of tannins by the keto-imide group of collagen, its basic groups partake in the fixation (30), probably mainly by hydrogen bond formation, although the participation of stronger valency forces may be involved (31). It has also been shown that the ratio of the amount of tannin held by the keto-imide groups to that fixed by the basic groups differs for the various tannins and with the experimental conditions, particularly pH value (31). Since the heat of reaction is different for the two types of binding, the temperature effect on the fixation of the tannins will also be influenced by this ratio. An important factor is, of course, the effect of temperature on the particle size of the tannins. On the whole, the results of Thomas and Kelly (29) conform to the general character of a process based on coordination by hydrogen bonding. However, in many instances of reactions involving the system of collagen-tannin solutions, the difficulty of distinguishing between rates of fixation and equilibrium fixation is appalling.

The difference between a hydrogen-bond-breaking agent, such as urea, and a compound, such as a polyphenol, interacting with and fixed by the

protein by hydrogen bonds, is one of degree only. In the former instance the electrostatic association of the urea molecule, in the state of resonance, concerns one keto-imide group, whereas some of the fixed tannins probably are attached to at least two protein groups, functioning as acceptors of the hydrogen bonds. This attachment of the molecule is probably further stabilized by the numerous electrostatic sites present in the conjugated aromatic nuclea (π-bonds), which are induced by resonance (32). These differences are revealed by the reversible uptake of urea by collagen on one hand and the partially irreversible takeup of tannin on the other hand. It is therefore of some importance to recall the view expounded by Küntzel (33) that the very same substance may destroy or preserve the protein, all according to the experimental conditions. For instance, an aromatic sulfoacid may exhibit tanning effects as an acid (pH 2–4) but exert hydrotropic (destructive) action on collagen in the form of the salt, such as sodium sulfonate (pH 5–8) in concentrated solution.

Formaldehyde tannage.—This tannage, on its usual application, with 1–2% formaldehyde in the pH range 6–8, is generally conceived to involve the basic protein groups, chiefly the ϵ-amino groups of the lysine residues. The main part of the bound aldehyde probably is present in the form of unipoint-bound methylol compounds (34), only a minor part being bipointly attached and functioning as a cross-linking agent (35). The reaction of formaldehyde with most other proteins is more complicated (36), particularly so with those possessing groups which in their reactions are temperature-dependent. This applies to proteins that are rich in amide groups. Fixation of the aldehyde by such proteins is not marked at temperatures up to 40° C., with the amino groups as the principal binding sites (37). However, at higher temperature, the formaldehyde fixation rises greatly when the amide groups commence to bind. This reaction is particularly prominent at high aldehyde concentration and low pH values (38). Since limed skin (pelt) contains comparatively few amide groups, and since, moreover, the conditions of reaction in the ordinary tannage are unfavorable for the amide function, this temperature-dependent reaction is not prominent. According to the only study of the temperature effect on formaldehyde fixation by collagen which has been carried out with the same substrate and identical experimental conditions (40), the reaction is comparatively little affected by temperature. In the pH range 6–8 a temperature increase from 0° to 20° C. has no effect on the aldehyde fixation by collagen. By a further rise, from 20° to 60° C., the increase of the binding amounts to 25% of the amount combined at 20° C. However, the reaction at pH values less than 4 is more temperature-dependent, the fixation of formaldehyde being almost doubled by a rise from 20° to 60° C. These findings may be explained by the additional aldehyde binding on the amide groups at low pH values, which reaction is favored by

temperature rise. In the clarifying paper of Highberger and Salcedo (25) the greater formaldehyde fixation by native hide powder compared to limed hide powder in the lower pH range was conceived to be due to the amide groups, which are more numerous in the native collagen. A major cause of the increased fixation of aldehyde by raising the temperature in the pH range 5–8 is probably the discharge of the ammonium ions of the protein, induced by temperature increase (41), by which additional NH_2-groups are made available to the formaldehyde.

Thermodynamics.—The heat of ionization of the different electrovalent protein groups, which is a governing factor in most ionic reactions, varies widely (41). Thus, the carboxyl ions of proteins have heat of ionization of the order of ± 1 kcal. per mole, while the heat of ionization of the electropositive groups is −12 to 13 kcal. per mole. That implies that the specific reaction of a stable, nonprotolyzing metal ion with the carboxyl ion should be practically independent of the temperature. On the other hand, the reaction of an anion of an acid with the charged basic protein groups should be lowered by raising the temperature, since it is an exothermic reaction.

An absolute condition for applying thermodynamic treatment to any system is that it should be in equilibrium and reversible (42). For two-phase solid-solution systems, with skin as the solid phase, the first requirement is not fulfilled for tanning agents as usually employed. Reversibility in its true sense is contradictory to tanning action, since the part of the agent which stabilizes the protein structure should be irreversibly fixed.

The reaction of dilute hydrochloric acid with collagen complies with both requirements, whereas the corresponding reactions of lignosulfonic and polymetaphosphoric acids meet the first condition, but only partially the second one. Larsson and the writer (43) have investigated these systems employing lightly formaldehyde-tanned hide powder at three different temperatures, 10°, 20°, and 30° C., in an attempt to correlate the degree of accessibility of the cationic groups of collagen to the anions of polyfunctional acids with data for heat of reaction. From the titration curves obtained on equilibrating the systems at the temperatures noted, the concentration of the acid in the external solution which is in equilibrium with the same amount of acid in combination with collagen at each of two different temperatures is obtained. By means of Clapeyron's equation, the values of $-\triangle H$ in kcal. per mole were derived. These values of $-\triangle H$ were about 1 for 0.1*N* hydrochloric acid and about 6–7 kcal. per mole for the lignosulfonic and polymetaphosphoric acids. The reaction of the strong acid with collagen was independent of the temperature, since discharge of the carboxyl ions of collagen is governing, while the uptake of the polyacids, which possess anions having affinity for the cationic protein groups, decreased with increasing temperature. Under such conditions, simple syntans of the sulfonic acid type would also be less reactive toward collagen on temperature increase.

The most thoroughly investigated compounds of this type are the acid dyestuffs, which usually are aromatic sulfonic acids. Their reaction with wool keratin is concerned in the dyeing process. The excellent hydrothermal stability of keratin is a great advantage in this connection. The physical chemistry of these important systems is treated lucidly by Vickerstaff in his informative monograph (44). While the affinity of sulfonic acids for proteins is diminished by temperature augmentation, the reverse holds true for the rate of fixation. In practice, as also in tanning, equilibrium is not attained as a rule. Hence, it is often contended erroneously that the affinity of the compound for the substrate is increased by raising the temperature. Fig. 2

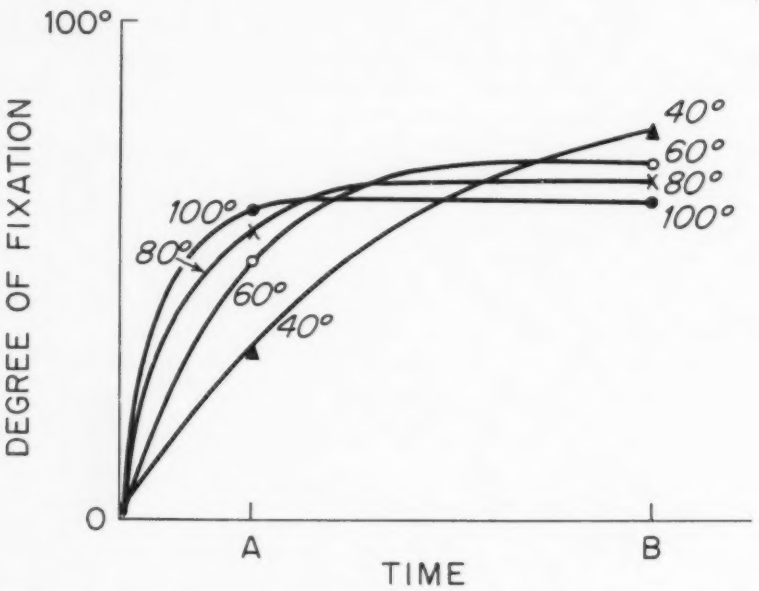


FIGURE 2.—The temperature factor in the fixation of acid dyestuffs by wool keratin as a function of time of interaction.

A: Rate of fixation

B: Equilibrium fixation

from Vickerstaff's book is included as a clarifying example (45). It shows the effect of the temperature of the bath on the rate and equilibrium of dyeing. It is evident that for short periods of treatment as used in practice, such as at time *A* in the graph, the uptake of the sulfonic acid dye, i.e., the rate of dyeing, increases markedly and regularly with temperature, whereas the binding capacity of keratin for the dyestuff, which is a function of the affinity

of the dyestuff anions for the electropositive protein groups, shown at *B* in the graph, is in the reverse order, being greatest for the series at 40° C. and smallest for 100° C. In dyeing, and in the fixation of aromatic sulfo acids by collagen, for instance, syntans, the arguments support the view that weak polar forces are set up between the resonating aromatic structure and the protein by hydrogen bonds or by other weakly polar interactions. These auxiliary forces appear to govern the fastness of the dyeing and the degree of irreversibility of the tannage (46). However, the reactions are initiated by the strongly electrovalent groups of the components of the system, i.e., the attraction of the negatively charged sulfonate by the positively charged protein groups. Thus, the hydrogen bonding does not contribute materially to the temperature function of polar molecules, although differences between constitutionally related sulfo-acids as to degree of stability of the compounds formed with proteins and concomitantly the temperature function are perhaps connected with the strength of these auxiliary forces. The displacement $-\overset{+}{N}H_3 \rightarrow -NH_2 + \overset{+}{H}$ of the protein by temperature increase, mentioned in another connection, will tend to lower the affinity further.

Chrome tanning.—The effect of temperature on ordinary chrome tannage, which represents a protolytic system, is exceedingly complicated. A number of factors, both additive and antagonistic, govern the influence of temperature on the fixation of the chromium complexes and their anions by the hide protein (47). As noted, the simple non-protolyzing metal cation, which is fixed only by the carboxyl ion of the protein, offers no problem, since the heat of ionization of that group is negligible. Hence, the reaction is practically temperature-independent. Moreover the shift of $-\overline{C}OO-$ groups to a $-COOH-$ group by temperature rise should tend toward a negative temperature coefficient (41). For such a decidedly irreversible system as basic chromium sulfate-collagen the thermodynamic approach may not be justified, particularly as the equilibrium constants of the carboxylic groups may change after partial inactivation by the cationic chromium complexes. However, such considerations are apparently only of secondary importance in this system in comparison with the dominating factor, the conditions of the solution of the chromium salt. The degree of protolysis of the basic chromium salt appears to govern primarily the course of the reaction (48). The investigation of the temperature function in chrome tanning carried out by Merrill and Schroeder (49) demonstrated the very pronounced effect of rise in temperature on the rate of chrome fixation by collagen (pickled pelt), resulting in a particularly sharp increase in the temperature range of 20°–40° C. This applies to the chrome fixation at equilibrium also (50). The protolysis of solutions of chromium salts is greatly favored by temperature increase, the ionization constant of water being augmented thereby. A number of aquo groups in the chromium complexes donate protons to the solution,

leaving a corresponding number of additional hydroxo groups in the complexes (47, 50). By olation of the hydroxo compounds thus formed, the chromium complexes are enlarged. Of course, the percent "over-all acidity" is not changed, only the distribution of the OH- and SO_4-groups (50). Thus, the thermal energy added will result in the formation of more basic and larger chromium complexes, and concomitantly the content of protons (acidity) will increase. Another alteration, to some extent antagonistic to the former, is the increasing formation of uncharged and anionic chromium complexes which is induced by heat (47, 48, 50).

Then—to size up the problem of the effect of heat on solutions of common basic chromium sulfates, excluding the extremely basic ones—the governing factor in promoting augmented chrome fixation by increasing temperature is the enlargement of the chromium complexes. In this instance with a polyelectrolyte, this implies greater equivalent weights of the chromium complexes combining with the collagen (51). The increased protolysis will to some minor extent militate against the former influence by competition of the protons with the cationic chromium complexes for the carboxyl ions of the protein. The dipolar-nonpolar shift of collagen will work in the same direction. The function of the electropositive protein groups would otherwise be expected to remain practically independent of the temperature (47, 50). Since the number of sulfate ions (belonging to the acid of protolysis and the anions compensating the cationic chromium complexes) associated with the electropositive protein groups remains constant, while the chromium complexes coordinated with the carboxylic groups contain increasing numbers of OH-groups as a consequence of the increased protolysis with temperature, the final result of tanning at higher temperature is increased basicity of the "chrome-collagen compound". This is the most important result in practice. The steric conditions of the collagen structure will affect the proportion of unipoint and multipoint binding of the chromium complexes, which factor probably plays an important role in this connection—a role only indicated and far from unravelled (51). In a recent paper by Kanagy (52) additional experimental support of this concept of the temperature factor in chrome tannage (48) has been given. Hydrogen-bonding forces are not involved in the common chrome tannage. However, reactions with nonionic protein groups, primarily the keto-imide group, by means of weaker valency forces have been indicated experimentally for certain chromium complexes (53).

Action of detergents.—In a number of processes in leather-making, reactions inherently associated with hydrogen bonding and similar electrostatic effects are encountered, for example, the swelling and labilization of hide proteins by solutions of detergents (54). The anionic type has attracted the main attention of the protein chemist. Lundgren and his associates (55) have shown that compounds such as sodium dodecylsulfate initially react

ionically with proteins through the electrostatic attraction of their anions by the electropositive protein groups. When multimolecular layers of negative charge are built up in the form of micelles, these micelles electrostatically repel negatively charged protein groups. Thereby, the hydrogen bonds are weakened and finally ruptured by the unfavorable steric conditions created. According to this concept, the swelling and labilization of the protein are secondary effects of the primary electrovalent reaction (55).

Recent studies of Otto and Loewe (56) are particularly interesting in the present context, since the concentration effect of the action of these detergents on collagen is stressed. Loewe (57) in unpublished work has drawn attention to the high degree of temperature dependence of the hydrotropic action of sodium dodecylsulfate on collagen. Thus, by a 10° temperature increase of 0.05*M* solution, from 20° to 30° C., the amount of collagen solubilized was increased tenfold. This electrostatic reaction resembles the hydrogen-bond-governed reaction of urea with collagen as far as the temperature factor is concerned. Both the compounds mentioned show marked labilization of the protein at room temperature when the protein is directly removed from the solution (54). On complete removal of the interacting agent the original properties of the collagen are practically restored, indicating a high degree of reversibility of the system (54).

FUTURE ASPECTS

The original work contained in this paper was performed during the "static" period of collagen chemistry. By the advent of the "dynamic" era the results and the problems outlined in this context will probably mean the appearance of additional problems. Some recent important discoveries on collagen behavior involve issues bearing on the present discussion. Thus, the gerontologist Verzár and his group (58) have found that upon the free shrinkage of rat tail tendon of *young* animals, some 40% of the original hydroxyproline residues of the collagen are released in the form of small polypeptides. This applies also to the skin of *young* mammals (private communication from Professor Verzár, 1960). Further, the remarkable contributions of Burton *et al.* (59), the Tunbridge school (60), Banga and Balo (61), and the aforementioned researches of Chvapil (7) will undoubtedly contribute to the problems under consideration. So also will the unravelling of the structure of tropocollagen and the reconstitution of collagens by Schmitt and his school (62), more particularly the most recent discoveries on the role of the endpolypeptide chains protruding from the tribelical macromolecule.

ACKNOWLEDGMENT

A grant from *The Swedish Technical Research Council* is gratefully acknowledged.

REFERENCES

1. Gustavson, *Biochem. Z.*, **311**, 347 (1942); *JSLTC*, **33**, 332 (1949).
2. Burk and Greenberg, *J. Biol. Chem.*, **87**, 197 (1930). Burk, *J. Biol. Chem.*, **120**, 63 (1937); **133**, 511 (1940).
3. Cohn and Edsall, *Proteins, Amino Acids and Peptides* (New York: Reinhold Publishing Corp., 1943) pp. 129–30, 144.
4. Pauling, *The Nature of the Chemical Bond* (Ithaca, N. Y.: Cornell University Press, 1940) pp. 212–13.
5. Katz and Weidinger, *Collegium*, **1933**, 75, 85.
6. Gustavson, *The Chemistry and Reactivity of Collagen* (New York: Academic Press, 1956) pp. 182–83.
7. Chvapil and Hruza, *Gerontologia*, **3**, 241 (1959).
   Chvapil and Zahradnik, *Study on Chemical Shrinkage and Relaxation of Collagen*, read as manuscript, to be published in *Biochim. Biophys. Acta*, 1960.
   See also: Bello, *Nature*, **185**, 241 (1960).
8. Thomas and Foster, *Ind. Eng. Chem.*, **17**, 1162 (1925).
9. Courts, in *Recent Advances in Gelatine and Glue Research*, ed. Stainsby (London: Pergamon Press, 1958) p. 145.
10. Gustavson, *Svensk Kem. Tidskr.*, **58**, 2 (1946); **63**, 167 (1951).
11. ———, *Ibid.*, **58**, 274 (1946); *JISLTC*, **30**, 264 (1946).
12. ———, *Svensk Kem. Tidskr.*, **56**, 14 (1944); *J. Colloid Sci.*, **1**, 397 (1946); *JALCA*, **47**, 151 (1952).
13. ———, *J. Am. Chem. Soc.*, **74**, 4608 (1952).
14. ———, *JALCA*, **41**, 47 (1946); *Acta Chem. Scand.*, **1**, 581 (1947).
15. ———, *Colloid Symp. Monograph, Vol. IV* (New York: Chemical Catalog Co., 1926) p. 79; *JALCA*, **21**, 206, 367 (1926); *Collegium*, **1927**, 466.
16. Huggins, *Proc. Natl. Acad. Sci. (USA)*, **43**, 209 (1957).
17. Gustavson and Holm, *JALCA*, **47**, 700 (1952). Gustavson, *Arkiv Kemi*, **13**, 107 (1958).
18. Batzer and Weissenberger, *Makromol. Chemie*, **7**, 320 (1952).
    Gustavson, *J. Polymer Sci.*, **12**, 317 (1954); *JSLTC*, **38**, 162 (1954).
19. Gustavson, *Svensk Kem. Tidskr.*, **66**, 359 (1954).
    Lasserre, *Bull. Assoc. Franc. Chim. Ind. Cuir*, **16**, 103 (1954).
20. Gustavson, *Discussions of the Faraday Soc.*, No. 16, 1954, p. 185; *Acta Chem. Scand.*, **1**, 581 (1947); **6**, 1443 (1952); **9**, 1049 (1955).
21. ———, *JALCA*, **41**, 47 (1946); Ref. (6) p. 215.
22. ———, in *Recent Advances in Gelatine and Glue Research* ed. by Stainsby (London: Pergamon Press, 1958) p. 259.
23. ———, in *Connective Tissue Symposium*, Council Int. Organization Medical Sciences", (Oxford: Blackwell, 1957) p. 170.
24. ———, *Svensk Kem. Tidskr.*, **52**, 261 (1940); *Kolloid Z.*, **103**, 43 (1943). However, cf. Theis, Ref. (40), pp. 372–73.
25. Highberger and Retzsch, *JALCA*, **34**, 131 (1939). Highberger and Salcedo, *JALCA*, **35**, 11 (1940); **36**, 271 (1944).
26. See Gustavson, *The Chemistry of Tanning Processes* (New York: Academic Press, 1956) pp. 244–82.
27. Mellon in *The Chemistry and Technology of Leather*, Vol. II, ed. O'Flaherty, Lollar, and Roddy (New York: Reinhold Publishing Corp., 1958) pp. 66–97.
28. Thomas and Kelly, *Ind. Eng. Chem.*, **16**, 31, 1925 (1924).
    Thomas and Foster, *J. Am. Chem. Soc.*, **48**, 489 (1926).
    Stecker and Highberger, *JALCA*, **37**, 226 (1942).
    See also Ref. (26), pp. 283–95.

29. Thomas and Kelly, *J. Am. Chem. Soc.*, **47**, 833 (1926).
Also see Wilson, *The Chemistry of Leather Manufacture* 2nd ed. (New York: Chemical Catalog Co., 1929) Vol. II, pp. 548–50; 580–81.
30. Ref. (26) pp. 160–77. Thomas and Foster, *J. Am. Chem. Soc.*, **48**, 480 (1926). Thomas and Kelly, *Ind. Eng. Chem.*, **18**, 625 (1926).
31. Ref. (26), pp. 160-75. Gustavson, *Svensk Kem. Tidskr.*, **53**, 324 (1941). Gustavson and Larsson, Hagglunds Festskrift, Stockholm, 1947, p. 99; *Svensk Papperstidn.*, **50**, 101 (1947).
32. See Otto. *Das Leder*, **4**, 1, 193 (1953).
33. Küntzel, in *Stiasny Festschrift*, ed. Gustavson (Darmstadt: Roether, 1937) p. 191. Küntzel and Schwank, *Collegium*, **1940**, 445, 489, and 500. Cf. Gustavson, *Svensk Kemisk Tidskr.*, **61**, 114 (1949).
34. Gustavson, *JISLTC*, **24**, 377 (1940); *Svensk Kem. Tidskr.*, **52**, 261 (1940); *J. Biol. Chem.*, 169, 531 (1947).
35. Wiederhorn, Reardon, and Browne, *JALCA*, **48**, 7 (1953).
Wright and Wiederhorn, *J. Polymer Sci.*, **7**, 105 (1951).
36. French and Edsall, *Adv. Protein Chem.*, **2**, 318 (1945); Ref. (27).
37. Wormell and Kaye, *Nature*, **153**, 525 (1944); *J. Soc. Chem. Ind.*, **64**, 75 (1945).
38. Fraenkel-Conrat and Olcott, *J. Am. Chem. Soc.*, **68**, 34 (1946); **70**, 2673 (1948). Fraenkel-Conrat, Cooper, and Olcott, *J. Am. Chem. Soc.*, **67**, 950 (1945).
39. Fraenkel-Conrat and Olcott, *J. Biol. Chem.*, **174**, 827 (1948).
40. Theis, in McLaughlin—Theis, *Chemistry of Leather Manufacture* (New York: Reinhold Publishing Corp., 1945) pp. 364–65.
41. Ebert, *Z. physik. Chem.*, **121**, 385 (1926). Ref. (3), p. 445.
42. See Ref. (3), p. 445.
43. Larsson and Gustavson, *JSLTC*, **39**, 107 (1955).
44. Vickerstaff, *The Physical Chemistry of Dyeing*, (London: Oliver and Boyd, 1950).
45. Ref. (44), p. 114. See Fig. 50 on p. 145.
46. Otto, *Das Leder*, **4**, 193 (1953); "Present Day Views on the Mechanism of Leather Dyeing", (Ludwigshafen: BASF., 1958).
47. Ref. (26), pp. 94–96.
48. Gustavson, *Collegium*, **1926**, 101. "Die Chemie der Chromgerbung", in Grassmann, *Handbuch der Gerbereichemie* (Vienna: Springer, 1939) II/2, pp. 251–53.
49. Merrill and Schroeder, *Ind. Eng. Chem.*, **21**, 1225 (1929).
50. Gustavson, *J. Phys. & Colloid. Chem.*, **51**, 1181 (1947); *JISLTC*, **31**, 181 (1947).
51. ———, *JALCA*, **48**, 559 (1953); *Arkiv Kemi*, **11**, 185, 423 (1957); *Nature*, **182**, 1125 (1958).
52. Kanagy, *JALCA*, **52**, 142 (1957).
53. Gustavson, *JSLTC*, **39**, 2 (1955).
54. ———, *Acta Chem. Scand.*, **4**, 1171 (1950); *JALCA*, **45**, 789 (1950).
55. Lundgren, *J. Am. Chem. Soc.*, **63**, 2854 (1941); *Textile Research J.*, **15**, 335 (1945); *Advances Protein Chem.*, **5**, 305 (1949).
56. Otto and Loewe, *Über Hydrotrope Wirkungen grenzflachenaktiver Stoffe auf die Hautsubstanz* (read in manuscript).
57. Loewe, *Das Leder*, **2**, 253 (1951). See also Ref. (56).
58. Meyer and Verzár, *Gerontologia*, **3**, 184 (1959).
59. Burton, Hall, Keech, Reed, Saxl, Tunbridge, and Wood, *Nature*, **176**, 966 (1955).
60. Hall, Tunbridge, *et al.*, *J. Gerontology*, **10**, 385 (1955).
61. Banga, Balo, and Szabo, *J. Gerontology*, **11**, 242 (1956).
62. Hodge, Highberger, Deffner, and Schmitt, *Proc. Natl. Acad. Sci.* (USA), **46**, 197 (1960).
63. Harrington and Schellman, *Compt. rend. Lab. Carlsberg, Ser. Chim.*, **30**, 167 (1957). Harrington and Sela, *Biochim. Biophys. Acta*, **27**, 24 (1958).

64. Klotz, *Science*, **128**, 815 (1958). Jacobson, *Svensk Kem. Tidskr.*, **67**, 1 (1955).
65. Harrington, *Nature*, **181**, 997 (1958). *Cf.* Schellman, C., and Schellman, J., *Compt. rend. Lab. Carlsberg, Ser. Chim.*, **30**, 463 (1958). See also Piez, *J. Am. Chem. Soc.*, **82**, 247 (1960); Burge and Hynes, *J. Mol. Biol.*, **1**, 155 (1959); and Kurtz, Berger, and Katchalski, E., *Nature*, **178**, 1066 (1956).

Received May 21, 1960.

EIGHT DEGREES IN GIVING

by Maimonides

He who gives grudgingly, reluctantly, or with regret.
He who gives less than he should, but gives graciously.
He who gives what he should, but only after he is asked.
He who gives before he is asked.
He who gives without knowing to whom he gives, although the recipient knows the identity of the donor.
He who gives without making his identity known.
He who gives without knowing to whom he gives, neither does the recipient know from whom he receives.
He who helps a fellow man to support himself, by a gift, or a loan, or by finding employment for him, thus helping him to become self-supporting.

Surely helping people by contributing The United Way attains the highest rung in the ladder of charitable giving.

Each fall millions of Americans join their United Fund, Community Chest, Good Neighbor Fund, or similarly named federated campaign, to help raise money to support vital voluntary health and welfare agencies. This efficient, simple method saves contributors and volunteers endless time and effort. Best of all, it makes more money available to the participating agencies, for they do not have to conduct overlapping, separate campaigns.

Boy and Girl Scouts, Camp Fire Girls, Visiting Nurses, Red Cross, Salvation Army, U.S.O., family agencies, services for the aged, the Y's, hospitals and clinics . . . we could go on and on listing the groups that benefit from these once a year United Community Campaigns. Furthermore, each agency participating in your United Fund or Community Chest has had its services and dollar needs screened and approved by a committee of citizen volunteers.

When your neighbor or coworker approaches you for your pledge, think of the many, many people who depend upon your United Way contribution, and give generously. It's a giant economy package!

LIFE LINES

Brief Biographies of Our Contributors

Miss Joan Anesey has been engaged in the collagen research carried out at Armour and Company since 1955. She received her B.S. degree from the University of Chicago in 1944 and then spent one year at Northwestern University on nephrosis research. She joined Armour and Company in 1945 and specialized in physical chemical measurements.

Jerome Cohen received his B.S. degree in Chemistry from Roosevelt University, Chicago, in 1944 and has been associated with Armour and Company for the past 15 years. His first work was on the preparation of pure enzymes. Since 1953 he has been studying the chemistry of collagen.

Dr. K. H. Gustavson is too well known to require an extended biographical note. He is universally recognized as one of the foremost leather chemists of our time. His chief interest is chrome tanning, but he has made numerous and important contributions to nearly every stage of leather manufacture. "Gus" spent some ten years in this country in the 1920's and early 1930's, during which period he was an active member of ALCA and a copious contributor to this *Journal*. He returned to Sweden in the mid-30's and is now Director of the Tanning Research Institute in Stockholm.

Dr. Arthur Veis received his Ph.D. degree in Physical Chemistry from Northwestern University. He then taught physical chemistry at the University of Oklahoma from 1950 to 1952. Dr. Veis joined the Central Research Laboratory of Armour and Company in 1952 and initiated a program of basic research in collagen, concentrating primarily on the collagen-gelatin transition and the behavior of the insoluble collagens. In September, 1960, Dr. Veis joined the Department of Biochemistry at the Northwestern University Medical School.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

OFFICERS

President—REUBEN G. HENRICH, Hiteman Leather Company, West Winfield, New York

President-Elect—ROBERT STUBBINGS, Milwaukee School of Engineering, Milwaukee, Wisconsin

Secretary-Treasurer—FRED O'FLAHERTY, Department of Leather Research, University of Cincinnati 21, Ohio

Council

FRANK A. EDMONDS, Cyanamid of Canada Limited, 5550 Royalmount Avenue, Town of Mount Royal, Que., Canada

HAROLD Y. MILLER, Seton Leather Company, 62 Verona Avenue, Newark, New Jersey

ROBERT M. LOLLAR, Armour Leather Company, Div. of Armour and Company, 401 North Wabash Avenue, Chicago Illinois

ELWOOD E. PRESLEY, Eagle-Ottawa Leather Company, Grand Haven, Michigan

HERBERT A. TETREAULT, SSUL Laboratory, A. C. Lawrence Leather Company, Peabody, Massachusetts

PAST PRESIDENTS

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. MCLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY, E. S. FLINN, E. B. THORSTENSEN, M. MAESER.

FIFTY-SEVENTH ANNUAL MEETING

The Fifty-seventh Annual Meeting of the Association will be held in Washington, D. C., at the Shoreham Hotel, August 20–25, 1961. This will be a joint meeting with the International Union of Leather Chemists Societies.

INVITATION FOR PAPERS TO BE PRESENTED AT THE MEETING OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

Host Society

The American Leather Chemists Association

August 20—25, 1961

Washington, D.C., U.S.A.

An invitation is herewith extended to leather chemists and tanners to submit manuscripts for presentation at the meeting of the International Union of Leather Chemists Societies.

Manuscripts should be sent to:

Dr. Wallace Windus

Eastern Utilization Research and Development Division
United States Department of Agriculture

600 East Mermaid Lane

Philadelphia 18, Pennsylvania
U.S.A.

The manuscript must be accompanied by a separate summary of not over 350 words suitable for inclusion in the program. It is requested that the summary be submitted in the three official languages of the International Union, namely English, French, and German.

The selection of the manuscripts for the "open" part of the program will be made by a committee composed of Dr. Wallace Windus, Chairman, Dr. Harold G. Turley, and Dr. Joseph R. Kanagy. Authors will be notified of the committee action through the Honorary General Secretary as early as possible.

In order to permit completion of work on the program it is imperative that manuscripts and summaries be received by March 1, 1961. Earlier receipt will be appreciated very much. Late arrival may prevent consideration for the limited space in this part of the program.

Papers should be of such a length that they can be delivered within a maximum time of twenty minutes. Shorter papers will be welcome. Ten

minutes will be allowed for discussion. These times are set to permit the inclusion of as many worthy papers as possible in the "open" program. Slides for projection should be in the standard lantern slide size of $3\frac{1}{4}$ x 4 inches.

Authors are reminded of the provision in the by-laws of the International Union requiring presentation of the paper in person. A manuscript may not be read by a non-author. It is understood that papers given at this Meeting will be submitted to an appropriate journal in the country of origin. If such a journal does not exist the host association will be pleased to extend the courtesy of publication in its journal.

A quarter of a century ago, the October, 1935, issue of *JALCA* reported with regret the death, on August 1, of Dr. Arthur D. Little, Chairman of the Board of Arthur D. Little, Inc. One-time president of the American Chemical Society (1912-14), Dr. Little opened a commercial laboratory in Boston in 1886 which in 1909 was incorporated under the name of Arthur D. Little, Incorporated, and in 1917 was moved to Cambridge. In 1931 he was awarded the Perkin Medal as "the American chemist who has most distinguished himself by his services to applied chemistry." Among his many professional affiliations, he numbered membership in the American Leather Chemists Association.

Technical papers appearing in the October, 1935, issue of *JALCA*, included the following:

The Influence of Some Sulphur-containing Tanning Materials on the Deterioration of Vegetable-tanned Leather by Sulphuric Acid, by Everett L. Wallace, Joseph R. Kanagy, and Charles L. Critchfield.

Evaluation of the Procter and Searle Method—Committee Report, by T. F. Oberlander, Chairman.

Water Absorption Capacity of Leather Committee Report—1935, by J. M. Seltzer, Chairman.

Extraction of Raw Tanning Materials Committee Report, by C. A. Blair, Chairman.

ABSTRACTS

Spruce Bark Tannin. X. Sulfiting Phlobaphenes of Spruce Bark Tannin. H. Endres, P. Stadler, and F. v. d. Crone. *Das Leder*, **11**, 1-4, discussion 5 (1960); see *JALCA*, **54**, 302 (1959).—There is a difference of opinion as to whether a sulfite extraction of spruce bark removes phlobaphenes or principally hemicelluloses, sulfited lignin, resins, etc. Extraction of a bark with water removed 9.6% of tannin, and a following sulfite extraction removed 1.8% for a total of 11.4% tannin, whereas a sulfite extraction removed 15.5% tannin. The latter was conducted as follows: 400 g. bark containing 10.4% of tannin was heated 30 min. at 100°C. with 1 l. water containing 10 g. sodium sulfite and 10 g. sodium bisulfite; it was then drained and washed with 1 l. has the same -CO-N- bonding as hide protein and synthetic polyamides and can unite to these by hydrogen bonds. It will remove both tannin and phlo-

baphenes from bark at room temperature. Phlobaphene was prepared by thoroughly extracting a commercial bark with DMF, evaporating the extract to dryness in a vacuum, then removing all water-soluble tannin by repeated treatment with warm water and removing the resin with chloroform. Polyuronides and hemicelluloses could not be identified in this pure, water-insoluble phlobaphene. It dissolved completely in a few minutes when treated at 70°–80°C. with the sulfite-bisulfite mixture (2.5% of each, phlobaphene basis). If the phlobaphene, however, was boiled in water for 1 hour before treatment with sulfite, only about 15% dissolved. This explains why a hot water extraction before the sulfite extraction reduces the total amount of tannin found in the bark. Three different extracts were prepared by leaching 2-kg. portions of bark with 20-l. portions of solvent for 24 hr. The solvents were DMF at 20°C. and at 50° and 1:1 DMF-water mixture at 50°C. The extracts were separated into (1) total extract, (2) a water-soluble fraction, and (3) a phlobaphene fraction which was sulfited. With these extracts cattlehide necks were vat-tanned for three months in liquors starting at 0.5°Bé and increasing to 7°Bé while pH was decreased from 6.8 to 3.8. The leathers were washed thoroughly, oiled on the grain, dried in the air, and rolled. Only the sulfited phlobaphene (3) had completely penetrated the hide; it made dark, firm leather. The water-soluble fraction (2) made bright, flexible leather, and the total extract (1) made dark, red-brown, rather firm leather. The degrees of tannage of the three leathers were (from 1 to 3) 69, 78, and 84; shrinkage temperatures were 72, 71, and 73; and water absorptions in 24 hours were 50.5, 47.5, and 40.5. Sulfited phlobaphenes are active tannins, have good affinity, and are comparable to the water-soluble tannin in tanning ability. The effect of sulfite on the water-soluble fraction was investigated by comparing the absorption on polyamide of weakly and strongly sulfited tannin with the unsulfited material. The affinity of the tannin for polyamide decreased when it was sulfited, and the decrease was proportionally greater as the amount of sulfite was increased. I.D.C.

Pigskin Leather as Natural Shrunken Leather. S. Nador, M. Mihajlavic, and P. Vuletic. *Das Leder*, **11**, 39–40 (1960).—Although pigskins are not considered suitable for shrunken leather, a shoe upper leather of this type can be made by a modification of the process used for making shrunken leather. Skins from straight-bristled, fleshy swine must be used, not those from fat animals. Bristles should be removed with a sulfide paste followed by 8 days in a strong sulfide liquor containing lime. The skins should then be cleaned, split, delimed, and bated. Careful control of liming and bating is required to avoid having soft parts of the skin too loose and the shell too stiff. The bated skins should be put into a bath of Irgatan LV strongly acidified with formic acid. The float should be very short. Drawn grain starts at once and is fixed by a strongly basic, cationic chrome liquor. The leather should be shaved, neutralized, treated with Tamol GA, colored, oiled, and hung to dry without airing or setting out. After finishing with a casein finish and drying, the leather should be boarded in 8 quarters. I.D.C.

Clarification and Bleaching Methods for Gelatin and Their Use on Gelatin Products from Chrome Leather Wastes. A. Steigmann. *Das Leder*, **11**, 12–15 (1960).—There is a growing demand for medium- or low-grade gelatins for use in pharmaceutical preparations, food products, etc. A mag-

nesium oxide (MgO) process for making such gelatin from chrome leather shavings is as follows: Neutralize 6.75 kg. shavings (moisture 48%, fat 2%) for 2 hr. in 25 l. water containing 100 g. MgO, then wash in running water for several hours. Heat the shavings in 20 l. water containing 300 g. MgO, and hold at 90°C. for 2 hr. to obtain the first extract (4%). Heat twice more for 3 hr. at 90°C., first with 18 l. water containing 100 g. MgO and then with 15 l. water containing 50 g. MgO. Boil the residue in 10 l. water, or heat it for 40 min. in an autoclave at 121°, and filter. The final residue can be used for recovery of dichromate. Combine the first three filtrates, filter, add kieselgur and active charcoal, filter, bleach at 50° for 30–45 min. with 100 ml. 7.5% peroxide, remove excess peroxide with sulfur dioxide gas until pH 6.0 is reached, evaporate to 20–30%, and refilter. A second reductive bleach with 0.5 g. per kg. sodium hyposulfite ($Na_2S_2O_4$) may be needed to remove darkening caused by evaporation. To clarify gelatin proceed as follows: To 100 kg. gelatin in 5% solution add 2 kg. MgO powder, 0.4 kg. calgon ($NaPO_3$) in 10% solution, and 0.4 kg. water-free potash alum, hold at 60°–65° until a flocculent precipitate forms (about 15 min.), add diatomaceous earth, and immediately filter and adjust to pH 6.0. Modifications of these methods are also given. I.D.C.

The Reaction of Animal Skin with Catechol and Formaldehyde. A Contribution to the Nature of Condensation Tanning. F. Stather, G. Reich, and R. Steinhardt. *Das Leder*, **11**, 5–10, discussion 11 (1960).—In condensation tannages a true chemical bond is formed by a condensation reaction between the tannin and hide substance. Windus made excellent leather which was stable to acid, alkali, or wetting by a condensation reaction with resorcin and pyrogallol. These materials are expensive, but catechol, which is cheaper and can be recovered from brown coal sulfur water, would not tan even at low pH values. Increasing reactivity by raising temperature has limited application, but increasing the resistance of the hide to heat by means of a pretannage with formaldehyde or with a chromium or aluminum salt was investigated as a possible method. The first two were not satisfactory, but a pretannage with aluminum sulfate resulted in a soft, full, light-colored leather. This method may find use as a tannage for soft leather or sweat-resistant insole leather, or as a rapid tannage for sole leather. To determine optimum conditions tannages were made with calfskins that had been painted with sulfide for 4 hr., limed two days, delimed with ammonium sulfate, and thoroughly washed. They were tanned at 40°C. in 200% floats, washed 30 min. in 500% water, treated with 15% ammonium sulfate in 500% water to remove all formaldehyde, washed twice, tacked out without tension, and dried at 20°–25°C. The tanning chemicals were added on the basis of the skin weight after it had been centrifuged for 15 min. (The quantities used were 10% and 15% catechol, 2 and 4 moles of formaldehyde per mole of catechol, and 3% and 13% aluminum sulfate). Volume yield (volume of leather containing 100 g. of hide substance), shrinkage temperature (Ts), and feel of the leathers improved as the time of tanning was increased from 8 to 24 hr. or the amount of formaldehyde was increased from 2 to 4 moles per mole of catechol. Increasing the amount of aluminum sulfate from 3% to 13% improved volume yield but did not raise Ts. If the amount of catechol was increased from 10% to 15%, yield decreased and leather quality was lowered. If the catechol was added first, followed by the formaldehyde and aluminum sulfate together, the leather

was softer, fuller, and had better feel than if either of the other materials was added first. Technical Diphen, a mixture of catechol and its methyl homologs, obtained from brown coal, was no more reactive than pure catechol. Ts was highest at the highest temperature used (50°C., 24 hr.) or for the longest times of tanning (72 or 96 hr. at 38°). In condensation tanning with catechol and formaldehyde the most important reaction is the chain coupling of catechol molecules by methylene bonds. This reaction is catalyzed by acid and is also affected by aluminum salts. The velocity of the reaction at 40°–50° is as great at pH 2.6–2.8 with aluminum sulfate as at pH 0.9 with sulfuric acid. Uncondensed catechol has some affinity for skin but has a hydrotropic action; it may soften the skin and lower Ts to 40°C. If more than 15% catechol is used the skin will shrink during tanning. Although there are indications of a Mannich reaction, it cannot be demonstrated. The Ts of catechol leather from a normal skin was not lowered by treatment with alkali, whereas that from deaminized skin was lowered from 75° to 58°. Semitechnical tanning tests showed that tanning and finishing could be by usual methods. The process is of interest for making sweat-resistant insole leather and for pretanning to speed the vegetable-syntan tannage of sole leather. Sole or insole leathers tanned entirely by this catechol process were flat and empty; calf and pigskin upper leathers were satisfactory in all respects except that water absorption was too great. In the discussion Vlimmeren stated that he had found an optimum tanning pH at 1 as had Windus but also another at pH 7.5. The authors have not tried tanning with catechol and aluminum sulfate without formaldehyde although it was pointed out that this might be possible. Physiological (poisonous) effects of uncondensed phenolic residues in the leather were not considered in this work but must be investigated. I.D.C.

Studies on the Enzyme Depilation of Hides and Skins. VIII. Effect of Protease Treatment on the Swelling Property of Collagen. H. Toyoda, A. Futami, and M. Kikkawa. *Bull. Japanese Assoc. Leather Technol.*, **6**, 23–27 (1960) (English summary).—Swelling curves from pH 1.5 to 12.5 were obtained for collagen, and for collagens modified by deamination, acetylation, mehylation, or pretreatment with lime liquor, trypsin, or *B. megatherium* 3E protease. Swelling capacity was diminished by deamination and by acetylation, while methylated collagen swelled greatly over most of the pH range. Pretreatment with lime increased swelling in alkaline solution. Pretreatment with trypsin or with *B. megatherium* 3E protease increased alkaline swelling but slightly decreased maximum acid swelling. *B. megatherium* protease was somewhat less effective than trypsin when used at the same gelatinase activity. Maximum alkaline swelling increased steadily with duration of protease pretreatment. H.B.M.

Nature of Tannins and Phenolic Nontans in Myrobalans (*Terminalia chebula*). K. J. Scaria and S. K. Barat. *Bull. Central Leather Research Inst., Madras*, **6**, 361–71 (1960).—An aqueous extract of crushed myrobalans nuts was subjected successively to horizontal electrophoresis in veronal buffer at 0.05 ionic strength, and to vertical chromatography in butanol–acetic acid–water (4:1:5). On drying and developing with ferricyanide–$FeCl_3$ reagent, 13 different phenolic constituents were detected. When the extract was pretreated with hide powder, 9 constituents were removed, and the other 4 were very little affected. When the extract was only partially detannized (by

using a small amount of hide powder), subsequent examination showed that the more mobile tannin components were preferentially taken up. Deaminated hide powder took up slightly less tannin but behaved the same as unaltered hide powder otherwise. From the electrophoretic and chromatographic behavior of corresponding pure compounds, chebulinic, chebulagic, and gallic acids, and corilagin were identified in the extract, while 3:6 digalloyl glucose and m-digallic acid were shown to be absent. Spectrophotometric studies of the components after elution showed that all components (in water) had absorption maxima at 237–40 mμ, and many had a second maximum at 275–78 mμ. The latter was suppressed by borate buffer. It is suggested that the 2 absorption maxima are produced by phenolic OH groups of different ionization constants. H.B.M.

The Influence of the Temperature of Crystallization on the Shrinkage Temperature of Collagen. S. Ghosh. *Bull. Central Leather Research Inst., Madras*, **6**, 377–79 (1960).—It is suggested that the lower shrinkage temperature of collagen from the skins of cold water fishes, compared to those living in warm water, may not be due, or not due entirely, to a difference in hydroxyproline content but rather to the difference in the temperature at which the collagen is formed ("crystallized"). Specimens of rat tail collagen were held in tension for 1 week at 8°C. and at 30°C. Five measurements of T_s gave values from 64° to 65°C. for collagen equilibrated at 8°C., and 65° to 68°C. for collagen equilibrated at 30°C. Rat tail tendons were shrunk thermally to destroy crystallinity, then held at 8°C. or 30°C. for 2–3 days and T_s was measured again. Values of T_s for specimens kept at 8°C. after the first shrinking varied from 15° to 20°C., while those for specimens kept at 30°C. were 36° to 40°C. These data support the idea that the temperature of habitat of fishes may have a profound effect on T_s of skin collagen. H.B.M.

Studies on Iron Tanning. I. Tanning Properties of the Complexes Formed between Ferric Iron and Organic Acid. Y. Inouye and H. Nihiro. *Bull. Japanese Assoc. Leather Technol.*, **6**, 8–14 (1960) (English summary).—Different amounts of formic, oxalic, malonic, succinic, adipic, glycolic, lactic, gluconic, or citric acid were added to $Fe_2(SO_4)_3$ solutions, which were then aged. Complex-forming powers of these anions were measured by determining the quantities of the acids required to prevent precipitation when the liquors were adjusted to pH 3.5 and 6.0 with NaOH. Pieces of skin were tanned, and tanning power was judged from the amount of sorbed Fe, T_s, and visual examination of the leathers. Formic and acetic acids have low complexing action but produced leathers of superior softness and fullness. The chelated complexes formed by oxalic and malonic acids are too stable to act as tanning agents. Ligands forming bridges between 2 Fe atoms form basic polynuclear complexes that can raise T_s. $Fe_2(SO_4)_3$ alone gave T_s 68°C. Maximum T_s attained with succinic or adipic complexes was 75°C. at pH 2.7 and was unaffected by further rise in pH. Hydroxy- and polyhydroxy carboxylic acids form basic Fe(III) complexes that are stable at the pH values required for tanning and produce rather soft, full leathers of much higher T_s. But these leathers are still unsatisfactory from the practical standpoint. The T_s decreases drastically as pH value is raised, and detanning occurs. With citrate complexes maximum T_s was 95°C. at pH 3.5, 90° at 4.0, 85° at 5.0, and 78° at 6.0. H.B.M.

Reversible Transformation of Gelatin to the Collagen Structure. A. Veis and J. Cohen, *Nature*, **186**, 720–21 (1960).—The conversion of soluble collagen to gelatin has been shown to involve the separation of the three-chain coiled-coil structure of the collagen molecule into single peptide chains, each having the disordered random-coil configuration. It was thought that if the relative peptide chain alignments were retained near the cross-linkage sites, treatments which induced the collagen fold might give rise to ordered collagen-like fibers. Native bullhide corium collagen was extracted at pH 6 in an isoionic suspension at 60°C. for 1 hour. The solution was filtered through sintered glass and then fractionated into 6 fractions by an ethanol-NaCl coacervation technique. The last 5 fractions were each dissolved in warm water, and the gelatin was precipitated with acetone. The solution and precipitation were repeated. The dried acetone precipitate from the third fraction was dissolved in 0.1*M* KCl at 40°C., the solution was clarified by centrifugation in the ultracentrifuge, and the clear solution was kept 20 hours at 4°C. The gel so formed was placed in a 40°C. bath and held there without shaking; as the gel melted, floccules appeared. This fibrous precipitate showed typical collagen cross-striations in the electron microscope and a characteristic periodicity averaging about 610 Å. The fibers represented about 10% of the third fraction. Only gelatins which had strong interchain cross-linkages yielded fibrous precipitates with this technique. C.L.D.

PATENTS

Waterproofing Leather. Brit. Pat. 826,065. Boehme Fettchemie G.m.b.H. Appl. May 10, 1957.—Leather is impregnated and waterproofed by contacting it with an organic solvent solution of a condensation product or mixture of an alcoholate of a polyvalent metal and an acid organic derivative of a phosphorous acid containing at least six carbon atoms. The polyvalent metal may be aluminum, titanium, zirconium or magnesium, and the alcoholate may be the ethylate, isopropylate, butylate, octylate or dodecylate, or one the alkyl constituent of which contains other substituents such as halogen or contains additional basic groups. Mixed alcoholates may also be used. Acid phosphorus acid derivatives which may be used include phosphoric acid monooctyl ester, monododecyl ester, monooleyl ester, monotetradecyl ester, monoalkyl phenol esters (alkyl residue C_4—C_{15}), mononaphthenyl ester, monoabietyl ester, and mixtures of such esters with the corresponding diesters or with esters which contain substituents of or are interrupted by hetero atoms or hetero atom groups. Instead of acid phosphoric acid esters, acid phosphoric acid alkylamides, or corresponding derivatives of alkylphosphonic acids or alkyl phosphinic acids may be used. The reaction is effected in the cold or by heating if necessary to 30–50°C. The preferred molar ratio of phosphorous acid ester to alcoholate is 0.5–1.5:1. The solvents used may be isopropanol, trichlorethylene, toluene, petrol, benzene or ligroin and the solutions may be used per se or

the solvent distilled off after completion of the condensation reaction and the residue used in solution in the oils used for oiling leather such as mineral oil, e.g. spindle oil. Small amounts of complex-stabilizers such as esters of hydroxycarboxylic acids, products with reactive methylene groups, hydroxy-oxo- compounds, acetylacetone, acetoacetic ester and oximes may be added to the solutions. The application may be by steeping, brushing or spraying. In a typical example, solutions of aluminum isopropylate and monododecyl phosphate in trichlorethylene are stirred together while heating and 0.1% of acetoacetic ester added as a stabilizer; the solution is adjusted to 3% content and sprayed on to dyed calf skins, or may be evaporated and the residue, dissolved in mineral oil, used for oiling the skins. Another example describes the use of a toluene solution containing 10% of the reaction product of aluminium propylate and monotetradecyl phosphoric ester, 10% of montan wax, and a small proportion of acetyl acetone.

Tanning with Glutaraldehyde. U. S. Pat. 2,941,859. M. L. Fein and E. M. Filachione, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Filed Apr. 8, 1959.—1. The process of tanning an untanned animal skin comprising treating the animal skin with glutaraldehyde, as the tanning agent, dissolved in an inert solvent selected from the group consisting of water and a lower aliphatic ketone, at a pH in the range of about from 2 to 10, until the animal skin is tanned.

Removing Dirt and Manure from Fresh Hides. Brit. Pat. 829,080. Stehling Co., C. H. Appl. Nov. 5, 1958.—Hides are prepared for tanning by a process wherein manure and dirt are removed from the fresh unsalted hide which is then fleshed and salted. The removal may be accomplished by striking the hair side with rotating blades, there being relative translatory motion between the hide and the blades. Preferably the rotating blades are curved so that the hide is also smoothed out while being cleaned.

Depilatory Paint. Brit. Pat. 828,686. Booth, H. Appl. Oct. 9, 1956.—A composition to be applied to the flesh side of skins as a paint for their dehairing, and especially for the removal of wool from sheepskins, comprises an aqueous mixture of a substantially lime-free alkali such as caustic soda, a relatively small amount of a water-soluble sulphide such as sodium sulphide, an inhibitor acting in the skin for the oxidation of the sulphide such as sodium sulphite, and a promoter acting on the wool or hair for the sulphide oxidation such as finely-divided iron, ferric oxide or china clay (containing iron compounds), which latter may act as a thickener. A separate thickener such as calcium carbonate and starch may be used.

Fatliquoring Leather. Brit. Pat. 828,665. General Aniline & Film Corporation. Appl. Nov. 15, 1957.—The invention comprises compounds of formulae

$$R_1—CONH—(R_2NH)_n—R_3NHCOR_1 \quad (1)$$

and

$$R_4R_5N—R_2—(NHR_2)_m—NHCOR_1 \quad (2)$$

wherein R_1 and R_4 are C_3 or C_4-γ-hydroxyalkyl groups, R_2 and R_3 are C_{2-4} alkylene groups, R_5 is a C_{1-20} alkyl, alkenyl, hydroxyalkyl, alicyclic (including abietyl), aryl, aralkyl or heterocyclic group (e.g. pyrrolidyl, piperidyl, morpholinyl, or imidazolidyl), R_6 is hydrogen or a C_{1-20} alkyl or hydroxyalkyl group, or R_5 and R_6 taken together with the nitrogen to which they are attached represent a heterocyclic ring (e.g. morpholine), m is an integer of from 0 to 4 and n is an integer from 1 to 4, are used in the fatliquoring of leather.

Alum Tannage. U. S. Pat. 2,942,930. F. P. Luvisi, Elkins Park, W. F. Happich, Jenkintown, M. V. Hannigan, Lafayette Hill, and C. W. Beebe, Roslyn, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Filed Nov. 7, 1958.—1. A process for tanning skins comprising impregnating the skins with a solution of a water soluble aluminum salt until the skins are tanned, and subjecting the tanned skins to the action of a water soluble material selected from the group consisting of homopolymer of acrylic acid, sodium polyacrylate and ammonium polyacrylate, to fix the aluminum salt in the tanned skins, and subjecting the thus tanned skins to an aqueous fat-liquoring treatment.

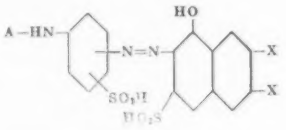
Tanning with Acetonylacetone. U. S. Pat. 2,938,763. E. H. Harris, Jr., and E. M. Filachione, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Filed Feb. 20, 1956.—1. A process comprising tanning hides with an aqueous solution containing acetonylacetone as the tanning agent at a pH of about from 7 to 11 for about from 1 to 3 days and then retanning the tanned hides with an aqueous solution containing a vegetable tannin.

Synthetic Tanning Agents. Brit. Pat. 825,503. Boehme Fettchemie G.m.b.H. Appl. June 29, 1956.—Tanning is effected by a water-soluble cationic resin containing a lipophilic residue, obtained by condensing (1) a water-soluble salt of an amine containing a lipophilic residue with (2) cyanamide or one of its derivatives, and (3) an oxocompound. (1) is preferably a primary, aliphatic, cyclo-aliphatic, aliphatic aromatic, aliphatic-cycloaliphatic amine salt whose lipophilic residue contains more than 6 and preferably 12–22 carbon atoms, e.g. coconut oil amine hydrochloride; (2) may be cyanamide, dicyandiamidine, guanidine, melamine, urea or preferably dicyandiamide; (3) may be formaldehyde or a substance yielding formaldehyde. The resins may be converted into water-insoluble forms by after-treatment with (a) anion-active synthetic soaps, anionic resins, anion-active compounds such as alkyl sulphates, sulphonates or benzene sulphonates the hydrocarbon residues of which contain 6–22 carbon atoms; (b) acid-reacting vegetable or synthetic tanning substances or resin tanning substances or their salts; (c) salts of inorganic, especially polymeric, acids, e.g. borates, phosphates and silicates; (d) acid, e.g. formic acid. The resins can be used alone or in combination with mineral, vegetable or synthetic tanning agents and as pre- or after-tanning agents.

Chrome-syntan Tanning Mixture. Brit. Pat. 827,430. Farbenfabriken Bayer A.G. Appl. Dec. 9, 1957.—A tanning mixture comprises one or more normal or basic trivalent chrome salts and one or more synthetic tanning

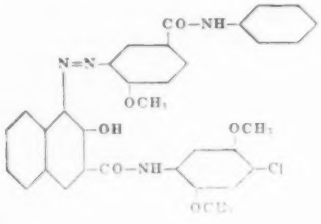
agents obtainable from methylol compounds of mono- or poly-valent phenols, polynuclear phenols or phenol resins by condensation with sulphites and/or bisulphites. The syntan may be produced in the presence of an alcohol or an aldehyde and/or a ketone (for preparation *see* Group IV (a)). The chrome salt may be chromium sulphate hexahydrate, chrome alum, potassium chromium sulphate or a self-reduced chromium tanning solution, such as reduced bichromate. The tanning may be finished with a vegetable and/or a synthetic tanning. The tanning mixture is usefully applied to the after-treatment of vegetable-tanned leather. Specifications 443,967, 478,280, 510,743, [*Group* IV], 595,337, 615,190, and 683,084, [*Group* IV (a)], are referred to.

New Monoazo-Dyestuffs. U. S. Pat. 2,906,748. H. Riat, Arlesheim, and F. Oesterlein, Basel, Switzerland, assignors to Ciba Limited, Basel, Switzerland, a Swiss firm. Appl. March 3, 1958. Claims priority, appl. Switzerland March 18, 1957.—1. A monoazo-dyestuff which in its free acid state corresponds to the formula



wherein A represents a β-halogenated propionyl radical, one of the two X's a hydrogen atom and the other a substituent R—CO—NH— in which R represents a member selected from the group consisting of the amino group and the radical of a lower aliphatic alcohol bound by its oxygen atom to the adjacent —CO—. Suitable for dyeing leather.

Monoazo-Dyestuff Insoluble in Water. U. S. Pat. 2,915,518. E. Fischer, Offenbach (Main), Germany, assignor to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt am Main, Germany, a corporation of Germany. No drawing. Appl. July 9, 1957. Claims priority, appl. Germany July 19, 1956.—The water insoluble monoazo-dyestuff corresponding to the following formula



May be used for dyeing leather.

Preservation of Hides. U. S. Pat. 2,937,921. T. C. Cordon, Philadelphia, C. W. Beebe, Roslyn, and F. P. Luvisi, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture. Filed Apr. 17, 1956.—A process of stabilizing and preserving hides prior to tanning

them comprising soaking green hides in an aqueous solution containing about from 10 to 20% of sodium chloride and having a pH of about from 4 to 6 until equilibrium between the hides and the solution is reached, removing the soaked hides from the solution, and then air-drying them.

Process of Reacting Protein with Isocyanic Acid and then with Aldehyde and Polymerized Product Prepared Therefrom. U. S. Pat. 2,923,691. H. H. Young, Western Springs, and E. F. Christopher, Chicago, Ill., assignors to Swift & Company, Chicago, Ill., a corporation of Illinois. Appl. Sept. 9, 1955.—1. A proteinyl urea-aldehyde copolymer prepared by reacting from about .1% to about 1.2% of an aldehyde, based on the weight of the protein solids, with a proteinyl urea at a pH of at least about 5, said proteinyl urea being formed by treating a protein with isocyanic acid whereby the free amino groups of said protein are converted to free carbamido groups.

Process of Dyeing Protein Fibers by Means of Insect Quinones. U. S. Pat. 2,936,210. R. K. Ladisch, Lansdowne, Pa., assignor to the United States of America as represented by the Secretary of the Army. Appl. April 14, 1955.—1. A process of dyeing wool which comprises making up a solution in the proportions of 80 ml. of water, 20 ml. of a neutral buffer solution, and 55 mg. of glycyl-DL-phenylalanine, immersing prepared wool in said solution, adding an aqueous solution of an ethyl-parabenzoquinone-containing quinone mixture obtained from flour beetles to the bath containing the wool, heating the bath slowly to approximately 98°C. and keeping the bath at that temperature for about 60 minutes, and removing the wool, rinsing and drying.

Depilating Predetermined Areas in Leather Preparation. U. S. Pat. 2,937,068. F. W. Panepinto, Philadelphia, Pa., assignor to William Amer Company, Philadelphia, Pa. a corporation of Pennsylvania. Original appl. March 11, 1958.—7. In a process for preparing leather including the steps of rehydrating a cured skin, removing the hair from the skin, and thereafter bating and tanning the skin, the improvement which comprises contacting only predetermined areas of the flesh side of the skin with an unhairing agent for a time sufficient for said unhairing agent to destroy the hair roots embedded within the contacted predetermined areas, removing the hair having the so-destroyed roots from the skin, and tanning the resulting skin whereby leather having hair only on predetermined areas thereof is produced, the hair-bearing and unhaired areas constituting the basis for a design pattern over the skin.

Patent Leather. U. S. Pat. 2,937,957. H. S. Lyness, 17 Carey St., Nahant, Mass. Filed May 22, 1958.—1. The method of finishing leather comprising applying a coating of a liquid japanning composition to a dyed black skin, then applying a coating comprising a solution of a polyamide of the nylon type in an inert solvent and causing it to dry, then applying a further coating of a japanning composition, and causing said coatings to dry to a glossy japanned finish.

BOOK REVIEW

Analysis of Fats and Oils. V. C. Mehlenbacher. The Garrand Press, Champaign, Ill., 1960. 640 pages. $12.00—The author of this book is Chief Chemist for Swift & Co. He has been Chairman of the Fat Analysis Committee of the American Oil Chemists' Society since 1939. As Editor of the Methods of the A.O.C.S. for five years, he rewrote the existing standard methods of that society. Finally, he and his associates have devised and published many new methods, now widely used. With this background as an originator, editor, and user of analytical methods, Mr. Mehlenbacher is ideally qualified for his avowed task of "bringing together such methods (standardized and non-standardized) and analytical information as are useful to the fat and oil analyst who is concerned with problems of production control and trading specifications." These qualifications have resulted in a volume that should become a classic in its field.

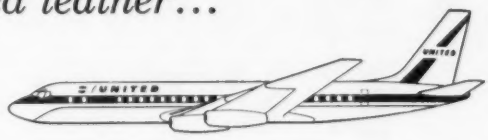
This is not to say that every leather chemist should own this book. The work is limited strictly to the analysis of natural animal and vegetable fats and oils, i.e., triglycerides of the higher fat acids. It is an indispensible book for oil chemists, but it contains much more than the average leather chemist needs to know about analyzing natural fats, and nothing on the analysis of manufactured fatty products—soaps, sulfated oils, and the myriad new synthetics—that are rather more important to the leather manufacturer. To have treated such materials with the same thoroughness would have required expansion of this work to two or more volumes. If this is ever done, we can at last transfer Lewkowitsch to the historical section of our libraries.

The book consists of eight chapters. The brief Introduction touches on the chemical structure of fats, classification of lipids, and refining of edible oils, and contains a valuable discussion of the standardization of methods. Next follows a very full chapter on the determination of Fat Content of oleaginous materials, including predrying, grinding, extraction, and estimation of the fat by weighing, refractometry, or other physical measurement. Chapter III deals with Estimation of Impurities (water and volatile matter, insolubles, acidity, unsaponifiables, ash, soap, metals, metalloids, hydrocarbons, and refining loss). Stability Tests are covered in Chapter IV, Specific Tests and Identification in Chapter V, Chemical Characteristics (saponification value, iodine values, and other methods of measuring unsaturation) in Chapter VI, Physical Characteristics in Chapter VII, and Composition in Chapter VIII. The treatment throughout is modern. Such instrumental techniques as emission and absorption spectroscopy, polarography and chromatography are included whenever they have been employed successfully in fat analysis. Nor are the older methods treated superficially; for example, the familiar determination of iodine value fills 20 pages, beginning with the theory of the measurement of unsaturation in general and ending with a micro adaptation of the Wijs method. In between, no less than eight different iodine value procedures are described in more or less detail, and critically compared. Statistical estimates of precision are furnished for nearly all the analytical methods in general use.

The author's style is clear and concise. Paper and typography are excellent, and printer's errors are very few. The oil chemists are in Mr. Mehlenbacher's debt for a much-needed and laborious task well performed. H.B.M.

A SKILLED HAND IN CHEMISTRY . . . AT WORK FOR YOU

United Air Lines pampers its passengers with Nopco®-treated leather... stronger, softer, longer lasting



Passengers ride with the luxury of leather aboard this United Air Lines Douglas DC-8 Jet Mainliner. Every bit of this leather was made stronger, softer, more uniform, pliable and durable by products of Nopco Chemical Company.

Leather men count on Nopco® know-how. With over 50 years' experience, Nopco supplies a broad range of chemicals for the tanning industry — fatliquors, anti-oxidant and masking agents, degreasing agents, emulsifiers and penetrants, sponging compounds . . . you name it. In addition, Nopco skills and facilities are available to help manufacturers meet special requirements. Write today to Tanning Oil Department.

NOPCO®

NOPCO CHEMICAL COMPANY

60 Park Place, Newark, N.J.

PLANTS: HARRISON, N.J. • RICHMOND, CALIF. • CEDARTOWN, GA. • LONDON, CANADA

TANNING EXTRACTS
AND DYEWOODS

With 90 years of continuous service to the tanning and dyeing industry, the J. S. YOUNG CO. has progressively expanded its facilities... anticipating the requirements of the entire industry... large and small operators, alike. We are importers, processors and manufacturers of practically every well-known, reputable tanning extract and dyewoods—for all branches of the industry... for leather, and for silk, wool and synthetic textiles. Our facilities have grown in capacity, flexibility and efficiency. Our skilled technicians and research facilities are at the service of the industry to help meet and solve individual problems... to meet specifications and requirements.

Manufacturers of the famous CHEMBARK natural tanning extracts and other special products, for the CHEMTAN CO.

WATTLE BARK — A YOUNG EXCLUSIVE!

Special quality Wattle Extract, *extracted directly from top-quality bark — in our own Baltimore plant.*

THE J. S. YOUNG CO.

2701-2755 BOSTON STREET • BALTIMORE 24, MARYLAND

- SUMAC
- QUEBRACHO
- FUSTIC
- HEMLOCK
- HEMATINE
- GAMBIER
- MYRABOLAMS
- OSAGE ORANGE
- WATTLE
- HYPERNIC
- DIVI-DIVI
- LOGWOOD
- TANNIC ACID
- CHESTNUT

SALEM OIL & GREASE CO.

Specialists in Tannery Oils

•

Salem, Massachusetts
U. S. A.

Mexico DF
Mexico

MOELLON DEGRAS

DRUEDING BROS. CO.
GOLDSBORO, N. C.

LEATHER TANNED WITH NCS BRAND WATTLE EXTRACT IS ALWAYS IN GOOD TASTE – *Produced from high grade bark; pure, untreated, unadulterated, it is second to none.*

Uniform Quality

Light in Color

Good Leather Yield

MORE THAN 40 YEARS OF EXPERIENCE and KNOW-HOW

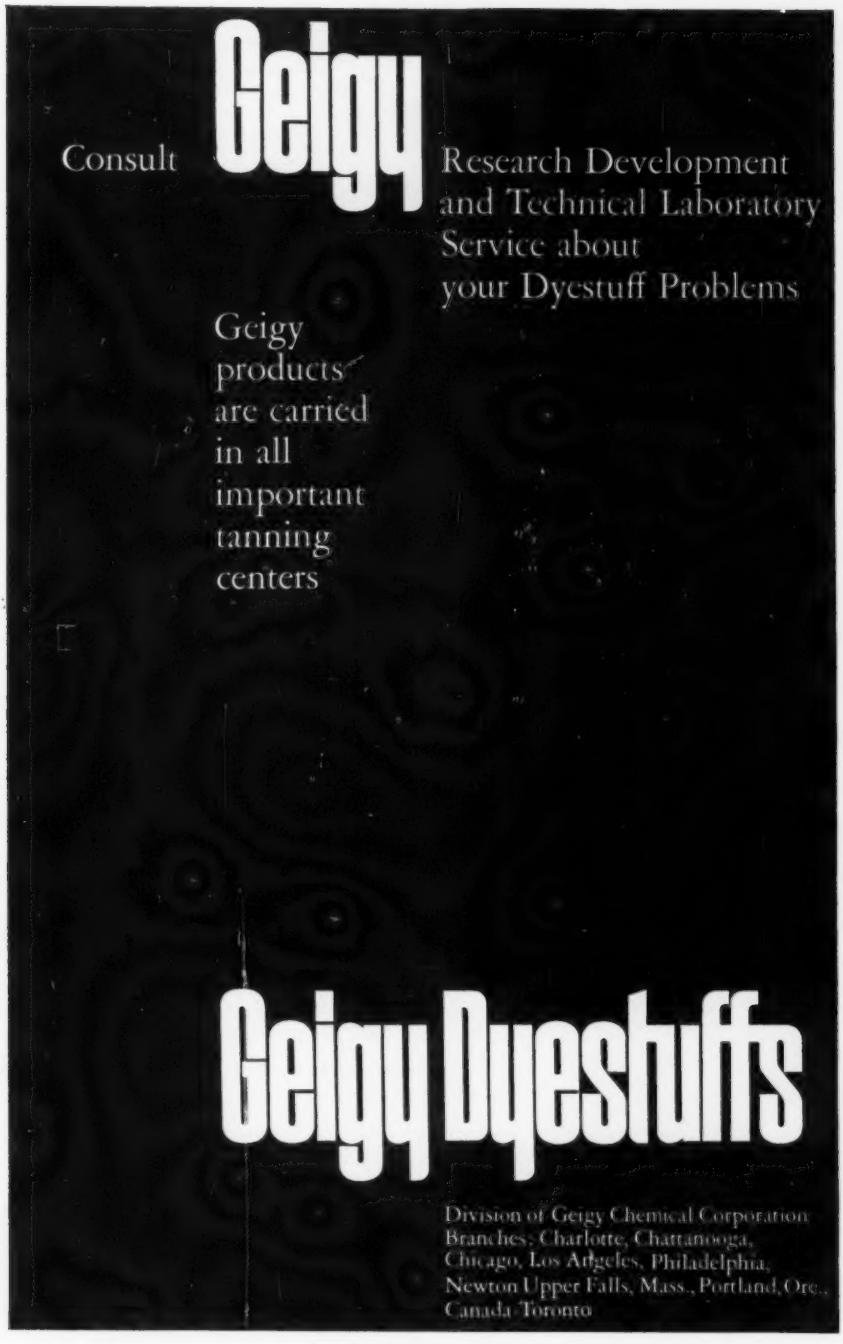
Use more WATTLE EXTRACT in your blend.
Specify NCS brand for superlative quality.

THE NATAL CHEMICAL SYNDICATE, LTD.
Maydon Wharf, Durban, Natal, South Africa

Distributors in United States and Canada

ELKAN-RIVER PLATE CORPORATION
27 William St., New York 5, N. Y.
Telephone WHitehall 3-6300

INTERNATIONAL PRODUCTS CORP.
625 Madison Ave., New York 22, N. Y.
Telephone PLaza 1-4770


Consult
Geigy
Research Development
and Technical Laboratory
Service about
your Dyestuff Problems
Geigy
products
are carried
in all
important
tanning
centers
Geigy Dyestuffs
Division of Geigy Chemical Corporation
Branches: Charlotte, Chattanooga,
Chicago, Los Angeles, Philadelphia,
Newton Upper Falls, Mass., Portland, Ore.,
Canada-Toronto

Fashion's newest shades in suede

ARE CONSISTENTLY BETTER WITH NATIONAL® LEATHER DYES

For best money-value and working properties, let us match your current suedes and splits with made-for-leather Para* Dyes and other National Dyes for Leather.

Our expert leather colorists will recommend economical combinations that are compatible for rate as well as depth of penetration, with excellent top-buffing and non-crocking qualities.

National Leather Dyes are strictly standardized, consistent batch after batch for more predictable results. Delivery is always fast from nearby stocks.

For prompt service, send your shades to our nearest leather laboratory today.

*Trademark of Allied Chemical

NATIONAL ANILINE DIVISION
40 RECTOR STREET, NEW YORK 6, N. Y.
Atlanta Boston Charlotte Chicago Greensboro Los Angeles
Philadelphia Portland, Ore. Providence San Francisco
In Canada: ALLIED CHEMICAL CANADA, LTD., 100 North Queen St., Toronto 18
Distributors throughout the world. For information:
ALLIED CHEMICAL INTERNATIONAL • 40 Rector St., New York 6, N. Y.

Allied Chemical

1st CHOICE

for Higher Quality Leather Production

Better Grading Figures!
Better Cutting Figures!
Overall Economy!

Extracts — Pancreatic Bates — Fillers
Sole Leather Finishes - Tanners Sugar
Tanners Lime — Chemicals

L.H. LINCOLN & SON, INC.
COUDERSPORT, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
154 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

JOHNSON · AND CARLSON

We Manufacture and Install

DRUMS - VATS - PADDLES - WOOD TANKS

Suppliers of V-Belts, Sprockets, Motors, Chain and Other Tannery Equipment

848 EASTMAN ST., CHICAGO 22, ILL.

KEPEC

KEPEC FINISHES · KCC CHEMICALS

CHEMICAL CORPORATION

MILWAUKEE 1, WISCONSIN

KEPECO • FINNALINE • KEPOLAC • EMULLO
KEEPASHINE • FONDO • UNI-LAK

(Reg. U. S. Pat. Off.)

MANUFACTURERS OF ALL TYPES OF

FINISHES FOR LEATHER

- LACQUER FINISHES
- WATER TYPE FINISHES AND DRESSINGS
- WATERPROOF LACQUERS

APEX CHEMICAL CO., INC.

Manufacturers of Chemicals since 1900

200 South First St. Elizabethport 1, N. J.

THE PERFECT BLEND "MIXER"

FOR HEAVY AND LIGHT VEGETABLE TANNED LEATHER

INCREASES YIELDS

"DRITAN" MYRABOLAM SPRAY-DRIED POWDER

IMPROVES COLOR

HIGHEST QUALITY ALWAYS

PRODUCED from Selected Fruit under Strict Chemical Control

END USE requirements more accurately assured

ELIMINATES old fashioned leaching — More Economical

Manufactured by
RICHARD HODGSON & SONS, LTD.
Beverley, Yorks, England

One of the world's largest manufacturers of Myrabolam Extracts.

The Pioneer of Tanning Extracts in Spray Dried Powder form for a quarter of a century.

other high quality "DRITAN" spray-dried powdered tanning extracts

QUEBRACHO
NEOCHEST
NEOMAC
WATTLE
AND BLENDS
WATTLE BLEACH
MANGROVE

Tanimex Corp.

97 WILLIAM STREET
NEW YORK 5, N. Y.
WHitehall 3-6300

YOU CAN RELY ON BAYOILS

- SULPHONATED OILS
- FAT LIQUORS
- WET and DRY FILLERS

Bay State Oil Products, Inc.

2 UNION STREET ❖ PEABODY, MASS. BAY STATE BRAND

• *Commonwealth* •

LABORATORIES, Inc.

CLI

Serving the Leather Industry since 1911

TECHNICAL SERVICE

CONSULTATION RESEARCH

Immediate Service on

HEAVY CHEMICALS — EXTRACTS — TANNERS OILS
DYESTUFFS — LEATHER FINISHES — SPECIALTIES
ABRASIVES AND COATED PAPERS.

COMMONWEALTH LABORATORIES, INC.

Gloversville, New York

There's More—Much More to choose from . . .

Extracts and Raw Tanning Materials from the Most Complete Line of Brands.

CHESTNUT
SOLID-SPRAY-DRIED
POWDERED

SOLID, CRUSHED OR SPRAY-DRIED POWDER
QUEBRACHO

Ordinary	Clarified
Granchaco	Bestsolubl
Indio	Rex
Sastre	Sol Puma
F. A.	
Puma	
Lutecia	

WATTLE

S. African	E. African
H. E. C.	Rhino
N. C. S.	
Comec	

SPECIAL SPRAY-DRIED EXTRACTS
DRITAN, R.W.D. — Wattle • Quebracho • Valonia • Myrabolams • Mangrove • Blends

Raw Tanning Materials
Myrabolams, Divi-Divi, Mangrove, Valonia, Sumac and Other Vegetable Tanning Materials from All Parts of the World.

TANIMEX CORP.— ELKAN-RIVER PLATE CORP.
27 William Street, New York 5 N. Y. WHitehall 3-6300

BONA ALLEN, INC.

Buford, Georgia

TANNERS SINCE 1873

•

Finest English Rein and Strap Leather

Latigotan Harness Leather

Manufacturers of genuine English type and full rigged hand tooled roping saddles.

COMET CHEMICAL CO., INC.

Plastic & Pigment Finishes
Topcoat, Plating & Glazing Lacquers
Vinyl Finishes for all types of Leather
Aniline Lacquers & Thinners

Lacquer Emulsions
Stable Trouble-free Water-tight
Clear, Black and White

Bigelow 3-1433-4

410 ADAMS ST., NEWARK, N. J.

BRANCH
COMET CHEMICAL COMPANY OF CANADA
56 MILL STREET - ACTON, ONTARIO, CANADA

THE STAMP OF DEPENDABILITY

VORTEXOL

SULPHONATED OILS and
FATLIQUORS — SUEDE SPRAYS
CROCK ELIMINATORS
WATERPROOFING SPECIALTIES

EASTERN INDUSTRIAL OIL PRODUCTS CO.

SAUGUS, MASS.

EASTERN OIL OF MEXICO PASEO DE LA REFORMA 95 MEXICO DF

EXPORT AGENT: WOLFF—INTERNATIONAL, Milwaukee, Wisconsin

HOWES LEATHER CO. INC.

SOLE LEATHER

•

SIDE LEATHER

•

Tanners Cut Sole Division

•

CUT SOLES

BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

L. H. HAMEL LEATHER CO.

Tanners of

Kid, Sheep and
Lambskin Linings

HAVERHILL, MASSACHUSETTS

Prime Leather Finishes Co.

188-194 S. 2nd St. R. 57 Grove St.
MILWAUKEE 4, WIS. SALEM, MASS.

Proctor **EQUIPMENT** for the **TANNING INDUSTRY**

- ROTO-SPRAY (4 or 8 Gun)
- PASTED LEATHER DRYERS
- TOGGLE DRYERS
- POLE AND HOOK TYPE CONVEYOR DRYERS
- SEASONED SKIN AND SPRAYED FINISH DRYERS
- WASHED CATTLE HAIR DRYERS

PROCTOR & SCHWARTZ, INC. Philadelphia 20, Pa.

REILLY-
WHITEMAN-
WALTON CO.

OILS of CHARACTER

CONSHOHOCKEN, PA.

Finishes
for all types of
Leather

FINE LEATHER FINISHES
NLF

NEWARK
LEATHER FINISH CO.

8 WILHELM ST. HARRISON, N. J.
Telephone HUmboldt 2-5072

NEW CHROMIUM COMPOUNDS
for the Progressive
TANNING CHEMIST

NUCHROME

Pure Basic Chromic Sulfate. No impurities, no sodium, aluminum or other salts.

DRY (35% Cr_2O_3)

LIQUID (25% Cr_2O_3)

CHROMIC CHLORIDE
CHROMIC ACETATE
CHROMIC FORMATE
CHROME ALUM AND OTHERS

FIBER CHEMICAL CORPORATION

P. O. BOX 218 MATAWAN, N. J.

Warner BELL-MINE LIME

You can depend on Warner Bell-Mine Lime
for uniform purity, analysis and physical properties.
Accurate laboratory control assures you
of consistently better milk of lime.

WARNER COMPANY
BELLEFONTE DIVISION, Bellefonte, Pa. • Philadelphia • Pittsburgh

OOC
Raw and Sulphonated
COD - SPERM - CASTOR
and NEATSFOOT OIL
OTTOL OIL CO. 455 Cortlandt St.
Belleville 9, N. J.

John B. Coyne
COYNE ENGINEERING AND EQUIPMENT COMPANY
Sales - Engineering - Service
TANNING MACHINERY
AUTOMATIC SWOBBING MACHINE
ALL TYPES LEATHER DRYERS
119 FOSTER STREET
PEABODY, MASS.

E. F. DREW & CO., INC.
BOONTON, N. J.
MANUFACTURERS OF
LEATHER OIL PRODUCTS

MANUFACTURERS OF
TANNERS' FINISHES
WEBER and SMITH, INC.
13 PIERCE STREET
READING, MASS.

CONSULTING SERVICE

Technical consultation is available for improving your leather, reducing your costs and developing new leathers and finishes. More than 40 years practical application of Scientific Research to Leather manufacturing.

ADOLF SCHUBERT, 549 W. Washington Blvd., CHICAGO, ILL.

BORNEO CUTCH EXTRACT
(MANGROVE BARK EXTRACT)
SAXE CUTCH CORPORATION
500 FIFTH AVENUE NEW YORK 36, N. Y.

PRESTO

The Original Dry Color for Splits and Suedes
(also in paste form)
COLOR COMPANY
WEST ALLIS 14, WISCONSIN
DRY COLORS • FINISHES

"ADE II TAN" **QUEBRACHO** **FILADE**
GAMBADE **EXTRACT** **DRIPASTE**

THE TANNADE COMPANY
2136 DOMINICK ST., CHICAGO, ILLINOIS

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

RACINE, WISCONSIN

92 South St., Boston, Mass., Day Gormley Leather Co. - 171 Madison Ave., New York City, Eugene Williams
41 E. Union St. Pasadena. Calif., David V. Whiting Co.

MORITE BRAND EST. 1908

MORITE BRAND

Sulphonated and Compounded

OILS

MORITE BRAND EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.

62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

THE MARSHALL LABORATORY

Mfg. American Standard Hide Powder

CONSULTATION LABORATORY SERVICES

P. O. Drawer 239 RIDGWAY, PA.

THE OHIO LEATHER CO.

Quality Calf Leather

LUXOR - BLACK JETTA
KAFFORITE - KOZY - JILL JETTA
EMBOSSED CALF - WHITE WASHETTE

TANNERY AND GENERAL OFFICES:
GIRARD, OHIO
BOSTON - NEW YORK - ST. LOUIS - CHICAGO

Garden State Tanning Inc.

Fleetwood, Pa.

Manufacturers of

Upholstery Leather

New York Office
12 EAST 33 STREET, NEW YORK 16, N. Y.

INDEX TO ADVERTISERS

ADOLF SCHUBERT XLII
ALLIED CHEMICAL CORP., National Aniline Division XXXII
ALLIED CHEMICAL CORP., Solvay Process Division ..... XVII—XXI
AMERICAN CYANAMID COMPANY, Dyestuff Department XXV
APEX CHEMICAL CO., INC. XXXV
ARKANSAS COMPANY, INC. XV
ARTHUR C. TRASK CO. VII
ARTHUR THOMAS CO. XXVI
ATLAS REFINERY XVI
BARKEY IMPORTING CO., THE XIII
BAY STATE OIL PRODUCTS XXXVI
BONA ALLEN, INC. XXXVII
CHEMICAL COATING MATERIALS CO. XVIII
CHEMTAN COMPANY ..... Outside back cover
COMET CHEMICAL CO., INC. XXXVII
COMMONWEALTH LABORATORIES, INC. XXXVI
COYNE ENGINEERING & EQUIPMENT CO. XLI
DIAMOND ALKALI CO. XII
DRUEDING BROS. CO. XXIX
EASTERN INDUSTRIAL OIL PRODUCTS CO. XXXVIII
E. F. DREW & CO., INC. XLI
ELKAN-RIVER PLATE CORP. XXXVII
EISENDRATH TANNING CO. XLIII
FIBER CHEMICAL CORPORATION XL
GARDEN STATE TANNING, INC. XLIII
GEIGY COMPANY, INC. XXXI
GENERAL DYESTUFF COMPANY ..... IX — X
HOOKER CHEMICAL CORP. III
HOWES LEATHER CO., INC. XXXVIII
INTERNATIONAL PRODUCTS CORPORATION ..... XXX—Inside Front Cover
INTERNATIONAL SALT COMPANY VIII
JOHNSON AND CARLSON XXXIV
KEPEC CHEMICAL CORPORATION XXXIV
LEATHER AND SHOES XXII
LEATHER MANUFACTURER, THE XXXIV
L. H. HAMEL LEATHER CO. XXXVIII
L. H. LINCOLN & SON, INC. XXXIII
MARDEN WILD CORPORATION V
MARSHALL LABORATORY XLIII
MEARL CORPORATION, THE XI
MOBIL OIL CO., INC. XXIII
NEWARK LEATHER FINISH CO. XL
NOPCO CHEMICAL CO. XXVII
OHIO LEATHER CO., THE XLIII
OTTOL OIL CO. XLI
PRESTO COLOR CO. XLII
PRIME LEATHER FINISHES CO. XXXVIII
PROCTOR AND SCHWARTZ, INC. XXXIX
REILLY-WHITEMAN-WALTON CO. XXXIX
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXIX
SANDOZ, INC. XIV
SAXE CUTCH CORPORATION XLII
SEABOARD CHEMICALS, INC. ..... Inside back cover
TANIMEX CORPORATION XXXV
TANNADE COMPANY XLII
TANNINS & CHEMICALS, INC. VI
TERRISS CONSOLIDATED INDUSTRIES XX
WALLERSTEIN COMPANY, INC. XIX
WARNER CO. XLI
WEBER & SMITH, INC. XLI
WHITTEMORE-WRIGHT CO. XLIII
WOLF, JACQUES & CO., A Subsidiary of Nopco Chemical Co. XXIV
YOUNG CO. J. S. XXVIII

How Tight Can You Get?

We visited a side leather tanner the other day who was wrestling with an old problem. He was trying to make a very soft straight chrome tanned side—pasted—in black and colors. As he went up percentage-wise in fatliquor using conventional sulfated oils, he finally got the softness he wanted, but by that time he had gone rag loose in the flank and belly areas of the side. The old dilemma!!

The Polarsol Approach

At this point, one of the Polarsols was introduced into the process as the fatliquor. These esterified oils seem to have the happy property of being able to produce very soft leather but, at the same time, very tight leather—a result not always obtainable with sulfated oils. Using less actual oil, this tanner now produces a butter-soft pasted side that is tight from backbone to belly.

Prove It to Yourself

Smooth, boarded and crushed softie sides for shoe upper and bag are a natural for the Polarsols. How tight can you get? Why not try the Polarsols on your pasted or toggled softie leathers and see for yourself. We'd like to send you a trial sample and complete information on how to use the Polarsols on your softie leathers. Just write or phone.

SEABOARD CHEMICALS, INC.

Dept. 101, 30 Foster St.

Salem, Massachusetts

In Canada: Tennant & Michaud, Ltd., Toronto and Montreal.

*new concepts of tanning
and retanning with Chemtan
M-1 and M-2

CHEMTAN COMPANY INC. EXETER, NEW HAMPSHIRE

All our facilities are devoted exclusively to the tanning industry